TURI
Toxics Use Reduction Institute
University of Massachusetts Lowell

Five Chemicals
Alternatives Assessment Study

Prepared by
The Massachusetts Toxics Use Reduction Institute
University of Massachusetts Lowell

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The Toxics Use Reduction Institute is a multi-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to promote the reduction in the use of toxic chemicals or the generation of toxic chemical byproducts in industry and commerce. Further information can be obtained by going to our website: www.turi.org, or by writing to the Toxics Use Reduction Institute, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854-2866.

Acknowledgements

Five Chemicals Alternatives Assessment Study

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List of Acronyms

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ACGIH	American Conference of Governmental Industrial Hygienists
AIM	Associated Industries of Massachusetts
AIHA	American Industrial Hygiene Association
ANA	American Neurological Association
ANSI	American National Standards Institute
APA	APA: The Engineered Wood Association
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
BCF	Bioconcentration factor
BOD/COD	Bio/Chemical oxygen demand
BTHC	Butyryl trihexyl citrate
CAAA	Clean Air Act Amendments of 1990
CARB	California Air Resources Board
CAS#	Chemical Abstract Service number
CCA	Chromated copper arsenate
CDC	Centers for Disease Control and Prevention
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
CERHR	Center for the Evaluation of Risks to Human Reproduction
CES	Centre Européen des Silicones (European silicone industry association)
CFC	Chlorofluorocarbon
ChV	Chronic value
CMC	Criteria maximum concentration
CNS	Central nervous system
CO_2	Carbon dioxide
CPSC	Consumer Product Safety Commission
CVD	Chemical vapor deposition
CWA	Clean Water Act
°C	Degrees Celsius
DCM	Dichloromethane or methylene chloride
DEHA	Di (ethylhexyl) adipate
DEHP	Di (2-ethylhexyl) phthalate
DEHPA	Di (2-ethylhexyl) phosphate
DEP	Department of Environmental Protection (Massachusetts)
DfE	Design for the Environment
DGD	Dipropylene glycol dibenzoate
DINCH	Di (isononyl) cyclohexane-1,2-dicarboxylate
DINP	Di isononyl phthalate
DEHT	Di(2-ethylhexyl)terephthalate
DHS	Department of Health Services
DOT	Department of Transportation

DPTB	Dipropylene glycol tertiary butyl ether
D5	Decamethylcyclopentasiloxane
EAC	Ethylene-acrylate-carbon
ECMO	Extra corporeal membrane oxygenation
EDTA	Ethylene diamine tetraacetic acid
EH&S	Environmental, health and safety
EO	Ethylene oxide
EOEA	Executive Office of Environmental Affairs (Massachusetts)
EPA	United States Environmental Protection Agency
EPI Suite	Estimation Program Interface Suite
ERP	Environmental Results Program
ESD	Electrospark deposition
EU	European Union
EVA	Ethyl vinyl acetate
FDA	Food and Drug Administration
GI	Gastrointestinal
GWP	Global warming potential
HAPs	Hazardous air pollutants
HC	Hydrocarbon
HCAT	Hard Chrome Alternatives Team
HCFC	Hydrochlorofluorocarbon
HESIS	Hazard Evaluation System and Information Service
HFC	Hydrofluorocarbon
HFE	Hydrofluoroether
Hg	Mercury
HCWH	Health Care Without Harm
HUD	Department of Housing and Urban Development
HVOF	High velocity oxy-fuel
IARC	International Agency for Research on Cancer
IDLH	Immediately dangerous to life or health
IRTA	Institute for Research and Technical Assistance
ISO	International Standards Organization
IV	Intravenous
Kb	Kauri-Butanol Value
Kd	Soil sorption coefficient
kg	Kilogram
Koc	Organic carbon adsorption coefficient
LC_{50}	Concentration that is lethal in 50% of the test animals
LCA	Life cycle assessment
LCSP	Lowell Center for Sustainable Production
LD_{50}	Dose that is lethal in 50% of the test animals
LEED	Leadership in Energy and Environmental Design
LNG	Liquefied natural gas
LOAEL	Lowest observable adverse effect level
Log K_{ow}	Octanol-water partition coeficient

List of Acronyms

LTAVD®	Low temperature arc vapor deposition
MACT	Maximum achievable control technology
MCL	Maximum contaminant level
MCTA	Massachusetts Chemistry and Technology Alliance
MDF	Medium density fiberboard
MDI	Methylene diphenyl diisocyanate
MEK	Methyl ethyl ketone
MEHP	Mono-ethylhexyl phthalate a metabolite of DEHP
mg	Milligram
NFPA	National Fire Protection Association
MSDS	Material safety data sheet
NDCEE	National Defense Center for Environmental Excellence
NESHAP	National Emission Standards for Hazardous Air Pollutants
NIC	National Interstate Council of State Boards of Cosmetology
NIOSH	National Institute for Occupational Safety and Health
NMP	N-methyl pyrrolidone
nPB	N-propyl bromide
NOAEL	No observable adverse effect level
NTP	National Toxicology Program
ODP	Ozone depletion potential
ODS	Ozone depleting substance
O&M	Operations & maintenance
OSB	Oriented strand board
OSHA	Occupational Safety and Health Administration
OTA	Office of Technical Assistance (Massachusetts)
PAE	Polyamide-epichlorohydrin
P2	Pollution prevention
Pb	Lead
PBT	Persistent bioaccumulative and toxic
PCB	Printed circuit board
PCBs	Polychlorinated biphenyls
PCDT	Poly-1,4 cyclohexylene dimethylene terephthalate
PCE	Perchloroethylene or tetrachloroethylene
PE	Polyethylene
PEL	Permissible exposure limit
Perc	Perchloroethylene
PET	Polyethylene terphthalate
PFC	Perfluorocarbon
phr	Parts per hundred resin
PIRG	Public Interest Research Group
PP	Polypropylene
ppb	Parts per billion
ppm	Parts per million
Prop 65	Proposition 65 (California)
PTFE	Polytetrafluoroethylene

PVC	Polyvinyl chloride
PVD	Physical vapor deposition
PWA	Printed wire assemblies
QA	Quality assurance
QC	Quality control
RCRA	Resource Conservation and Recovery Act
REL	Recommended exposure limit
RoHS	Restriction on certain Hazardous Substances Directive (European Union)
SAB	Science Advisory Board
SEHSC	Silicones Environmental, Health and Safety Council of North America
SERDP	Strategic Environmental Research and Development Program
SF	Substitution factor
SFI	Sustainable Forestry Initiative
SGE	Substituted aliphatic glycol ethers
SIAJ	Silicones Industry Association of Japan
SIC	Standard Industrial Classification code
SMC, D or T	Surface mount component, device or technology
SNAP	Significant New Alternatives Policy
SSL	Surface Solutions Laboratory (TURI)
STEL	Short-term exposure limit
TCA	1,1,1-trichloroethane or methyl chloroform
TCA	Total cost accounting
TCE	Trichloroethylene or trichloroethene
TCF	Totally chlorine-free
TLV®	Threshold limit value
TOP	Tri (2-ethylhexyl) phosphate
TOTM	Triethylhexyl trimellitate
TPN	Total parenteral nutrition
TPU	Thermoplastic polyurethane
Trans-DCE	Trans-dichloroethylene
TURA	Toxics Use Reduction Act of 1989 (Massachusetts)
TURI	Toxics Use Reduction Institute (Massachusetts)
TURI Lab	Toxics Use Reduction Institute Surface Solutions Laboratory
TWA	Time-weighted average
TWI	Taber Wear Index
UV	Ultraviolet
VCT	Vinyl composition tile
VHN	Vickers Hardness Number
VMS	Volatile methylsiloxane
VOC	Volatile organic compound
WEEE	Waste Electrical and Electronic Equipment Directive (European Union)
μg	Microgram

Table of Chemicals Studied

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Chemical	CAS Number
Lead	**7439-92-1**
4,4 Isopropylidenediphenol	80-05-7
Aluminum	7429-90-5
Barium stearate	6865-35-6
Bismuth	7440-69-9
Calcium hydroxide	1305-62-0
Calcium silicate	1344-95-2
Copper	7440-50-8
Iron powder	7439-89-6
Magnesium aluminum hydroxide carbonate hydrate	11097-59-9
Magnesium oxide	1309-48-4
Magnesium zinc aluminum hydroxide carbonate	169314-88-9
Polypropylene	9003-07-0
Quartz	14808-60-7
Steel	12597-69-2
Tin	7440-31-5
Titanium dioxide	13463-67-7
Tribasic lead sulfate	12202-17-4
Tungsten	7440-33-7
Zinc	7440-66-6
Zinc stearate	557-05-1
Formaldehyde	**50-00-0**
Urea	**57-13-6**
2-Bromo-2-nitropropane-1 (bronopol)	52-51-7
Acetone	67-64-1
Aluminum oxide	1344-28-1
Aqueous solution of a cationic amine polymer -epichlorohydrin adduct	
Calcium sulfate dihydrate (gypsum)	7778-18-9
Cellulose fiber (pulp)	9004-34-6
Copper compounds	7440-50-8
Diazolidinyl Urea	78491-02-8
Dicalcium silicate	10034-77-2
Diethylene Glycol Phenol Ether	104-68-7
Epichlorohydrin	106-89-8
Ethylene glycol phenyl ether	122-99-6
Glutaraldehyde	111-30-8
Methylene Diisocyanate	101-68-8
Nickel	7440-02-0
Paraffin wax	8002-74-2
Phenol	108-95-2
Polypropylene (PP)	9003-07-0
Portland cement	65997-15-1
Propylene Glycol	57-55-6
Sodium hydroxide	1310-73-2
Soy flour	
Tetracalcium aluminoferrite	12068-35-8

Chemical	CAS Number
Tri Sodium Citrate	68-04-2
Tricalcium aluminate	12042-78-3
Tricalcium silicate	12168-85-3
Wood fibers	
Zinc Sulfate	7733-02-0
Perchloroethylene	**127-18-4**
1,1,1,3,3-pentafluorobutane	406-58-6
2,3-dihydrodecafluoropentane	138495-42-8
2−Butoxy Ethanol	111-76-2
2-Butoxyethanol	111-76-2
Acetone	67-64-1
Alkyloxy polyethylene oxyethanol	84133-50-6
Aromatic Petroleum Distillates	64742-95-6
Azeotrope of substituted Aliaphatic Gylcol Tertiary Butyl Ether	132739-31-2
C9-C12 hydrocarbons	64742-88-7
Decamethyl Cyclopentasiloxane	69430-24-6
Diethylene Glycol Monoethyl Ether	111-90-0
Dimethyl Ether	115-10-6
Dimethyloxypropane	77-76-9
D-Limonene	5989-27-5
Heptane	142-82-5
Hexa-methyldisiloxane	107-46-0
Isobutane	75-28-5
Kerosene	8008-20-6
Liquid carbon dioxide	124-38-9
Medium Aliphatic Petroleum Solvent	64742-47-8
Methanol	67-56-1
Methyl Esters of C16−C18 and C18 Unsaturated Fatty Acids	67762-38-3
Nonyl Phenol Ethoxylate	9016-45-9
n-Propyl bromide	106-94-5
Orange Peel Oil Sweet Cold Pressed	8028-48-6
Petroleum Distillates	68551-15-5
Petroleum Sulfonate	78330-12-8
Poly dimethylsiloxane	63148-62-9
Propane	74-98-6
Propanol, (2-methoxymethylethoxy)	34590-94-8
Propylene glycol	57-55-6
Refined Soybean Oil	8001-22-7
synthetic hydrocarbon	64742-48-9
Toluene	108-88-3
Trans-1,2-dichloroethylene	156-60-5
Xylene	1330-20-7
Hexavalent Chromium	**18540-29-9**
Ammonium bromide	12124-97-9
Ammonium chloride	12125-02-9
Ammonium formate	540-69-2
Ammonium hydroxide	1336-21-6
Boric acid	10043-35-3
Butanedioic acid, sulfo-, 1,4-bis(1,3-dimethylbutyl) ester, sodium salt	2373-38-8
Calcium carbonate	471-34-1
Calcium molybdate	7789-82-4
Chromic sulfate	10101-53-8
Cobalt	7440-48-4

Table of Chemicals Studied

Chemical	CAS Number
Ethanol	64-17-5
hydrochloric acid	7647-01-0
Iron	7439-89-6
Nickel	7440-02-0
Potassium chloride	7447-40-7
Sodium sulfate	7757-82-6
Titanium	7440-32-6
Trivalent chromium Cr(III)	16065-83-1
Tungsten carbide	12070-12-1
Zinc	7648-85-7
Zinc molybdate	61583-60-6
Zinc oxide	1314-13-2
Zinc phosphate	7779-90-0
Zirconium	7440-67-7
DEHP, di (2-ethylhexyl) phthalate	**117-81-7**
79A, di linear C7C9 adipate	68515-75-3
ATBC, o-acetyl tributyl citrate	77-90-7
BBP, butylbenzyl phthalate	85-68-7
BOP, butyl, 2-ethylhexyl phthalate	85-69-8
BTHC, butryl trihexyl citrate	82469-79-2
DBP, dibutyl phthalate	84-74-2
DBS, dibutyl sebacate	109-43-3
DCP, di(2-normal-octyl) (aka capryl)	111875
DDP, isodecyl, diphenyl phosphate	29761-21-5
DEGDB, diethylene glycol dibenzoate	120-55-8
DEHA, di ethylhexyl adipate	103-23-1
DEHPA, di (2-ethylhexyl) phosphate	298-07-7
DEHT, di (ethylhexyl) terephthalate	6422-86-2
DGD, diethyl glycol dibenzoate	27138-31-4
DHP, di(isohexyl) phthalate	68515-50-4
DIDA, diisodecyl adipate	27178-16-1
DIDP, diisodecyl phthalate	68515-49-1
DIHP, di(isoheptyl) phthalate	71888-89-6
DINA, diisononyl adipate	33703-08-1
DINCH, di isononyl cyclohexane carboxylate	166412-78-8
DINP, di isononyl phthalate	68515-48-0
DIOA, di isooctyl adipate	1330-86-5
DIOP, di(isooctyl) phthalate	27554-26-3
DITDP or DTDP, di-isotridecyl phthalate or ditridecyl phthalate	68515-47-9
DIUP, di(isoundecyl) phthalate	85507-79-5
DOS, dioctyl sebacate	122-62-3
DUP, diundecyl phthalate	3648-20-2
ESBO or ESO, epoxidised soybean oil	8013-07-8
NODTM, tri(n-C8, C10)trimellitate	68515-60-6
OET, 2-ethylhexyl epoxy tallate	61789-01-3
OTSA, o-toluene sulfonamide	88-19-7
TCP, tricresyl phosphate	1330-78-5
TEGDB, triethylene glycol dibenzoate	120-56-9
TINTM, tri(isononyl)trimellitate	53894-23-8
TIOTM, tri(isooctyl)trimellitate	27251-75-8
TOP, tri octyl phosphate	78-42-2
TOTM, tri ethylhexyl trimellitate	3319-31-1
TXIB, butane ester (2,2,4-trimethyl 1,3-pentanedioldiisobutyrate)	6846-50-0

Executive Summary

Five Chemicals Alternatives Assessment Study

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Overview

In July 2005, the Commonwealth of Massachusetts requested that the Toxics Use Reduction Institute perform an alternatives assessment for five chemicals: lead, formaldehyde, perchloroethylene (PCE), hexavalent chromium, and di(2-ethylhexyl) phthalate (DEHP). For each chemical, the Institute was charged with identifying significant uses in manufacturing, consumer products, and other applications; reviewing health and environmental effects; and evaluating possible alternatives. The Institute was also directed to evaluate possible effects on Massachusetts employment and economic competitiveness associated with adoption of alternatives. The study was conducted within a single fiscal year, and had a total budget of $250,000.

Rather than attempt to study all uses of each chemical, the Institute selected priority categories of use for each chemical. Likewise, for each use studied, the Institute chose a subset of possible alternatives for analysis. The Institute analyzed a total of sixteen different use categories and approximately one hundred different alternatives.

This report presents factual information on each alternative. The study does not provide a ranking of the alternatives; rather, it provides information that will allow users to make informed decisions and, in some cases, to design additional research to fill remaining information gaps. An important aspect of this alternatives assessment is its transparency: all information collected by the Institute is available for users to assess in the context of their specific applications, concerns and needs. Where the Institute was not able to obtain full information for a given parameter, this is clearly noted.

The results of this study will serve as a guide for those seeking safer substitutes to the five chemicals discussed here. In every case, at least one alternative was identified that was commercially available, was likely to meet the technical requirements of many users, and was likely to have reduced environmental and occupational health and safety impacts compared with the base chemical. In addition, the methodologies piloted in this study should prove useful as a model for future efforts at alternatives assessment. Alternatives assessment is a relatively new and highly promising methodology for analyzing products and processes that affect human health or the environment. The present study helps to demonstrate the viability of alternatives assessment as a useful tool to support decision-making about chemicals and their alternatives.

Approach and Methodology

During the year, five teams of Institute staff and outside experts performed parallel alternatives assessments using a common process and methodology. The project was divided into three phases. In the first phase, the Institute identified uses of the five chemicals within Massachusetts, and prioritized a subset of those uses to analyze in depth. In the second phase, the Institute identified alternatives and, again, chose priority alternatives for further study. In the third phase, the Institute conducted detailed research on each of the priority alternatives, gathering information on the health and environmental, technical, and economic aspects of each alternative. For each phase of the analysis, the Institute relied on information from experts and publicly available resources. The Institute also consulted extensively with stakeholders, including industry representatives, government agencies, and public health, environmental and labor advocates.

Prioritization of Chemical Uses

Each of the five chemicals considered in this study has a wide range of uses. The Institute selected a subset of these uses based on the importance of each use in Massachusetts, the potential availability of alternatives, the extent of possible exposures for workers and the general population, and the potential utility for Massachusetts businesses and citizens of the alternatives assessment. To maximize the value of this pilot project, the Institute also made an effort to include a mix of uses relevant for industry, small business, and consumer products. The Institute placed a low priority on uses where alternatives are already being readily adopted, or where significant research on alternatives is being carried out by others.

For hexavalent chromium and DEHP, the uses selected for this study represent a large percentage of total use of these chemicals in Massachusetts manufacturing. Lead and formaldehyde, on the other hand, have a multitude of uses beyond those examined here. For perchloroethylene, the study incorporated uses of particular relevance for small businesses and consumer exposures. The assessments conducted for this study can be used as a model for future assessments of other uses.

Prioritization of Alternatives

Alternatives to toxic chemicals may include drop-in chemical substitutes, material substitutes, changes to manufacturing operations, changes to component/product design, and other technological or market solutions. The Institute identified more than 200 possible alternatives for the chemical uses of interest, then applied a health and environmental screen to all alternatives. The screen excluded any chemical that was a known or probable human carcinogen, failed a persistence, bioaccumulation, and toxicity (PBT) screen, or was included on the 1999 More Hazardous Chemicals list developed by the Massachusetts Toxics Use Reduction program's Science Advisory Board. Of the options that passed this initial screening, the Institute prioritized alternatives for further study based on additional information about viability, health and environmental effects, economic considerations, and importance to stakeholders. The Institute also chose to prioritize products or materials manufactured in Massachusetts. When several alternative chemicals or materials could be grouped together, the Institute selected a representative of that grouping for detailed consideration.

The individual chapters provide detailed information on the process by which the Institute chose the list of alternatives to assess for each chemical use. It is important to note that inclusion of an alternative in the assessment does not imply an endorsement of that alternative. Similarly, exclusion of an alternative from the assessment does not imply that it has been rejected. In some cases, alternatives have been excluded from this assessment simply because they have been studied in depth in another context.

Some alternatives, particularly those comprised of single chemicals, were assessed as generic alternatives. Other alternatives vary considerably depending on the precise formulation or manufacturer. In these cases the Institute assessed a representative product. The choice of a particular manufacturer’s product as representative does not constitute an endorsement of that product, or indicate that other similar products are not worthy of consideration.

Alternatives Assessment

The alternatives assessment included consideration of health and environmental effects, technical feasibility, and financial feasibility.

- **Health and environmental effects.** The Institute evaluated a subset of environment, health and safety (EH&S) endpoints. The Institute did not perform a detailed toxicological review for each alternative. Rather, the study relied on information obtained from authoritative bodies, emphasizing the most recent validated data or data that has been referenced by a US government agency. Where this type of information was not available, or where more recent studies called into question the results previously published by authoritative bodies, supplementary information was noted. The Institute relied on the U.S. EPA PBT Profiler software to gain information on persistence, bioaccumulation potential and toxicity. In cases in which it was necessary to evaluate chemicals in mixtures, the assessment considered each of the chemical constituents, excluding those making up 1% or less by mass of the mixture.
- **Technical feasibility.** The study identified and assessed application-specific performance requirements that must be met for each feasible alternative. The performance information that the Institute was able to obtain varied considerably among uses. For some uses information was obtained from published studies or directly from technical experts or several users of the alternatives. For other uses the Institute relied on information provided

by product manufacturers. The type of performance information that was available for a given alternative will affect the degree and nature of follow-up that may be necessary for users to draw conclusions about technical feasibility for individual applications.

- **Financial feasibility.** Data sources for financial information included manufacturers, stakeholders, the Chemical Economics Handbook and other standard reference sources. In many cases, particularly for emerging alternatives, no hard cost information was available. In other cases, sufficient cost information exists to conclude that the alternative is either more or less costly than the current chemical use. The Institute recognizes that cost comparisons today may be of limited relevance for emerging technologies and technologies that are gaining in popularity, since learning curves, economies of scale, and other factors can reduce costs over time.

It is important to note that this study was not designed to assess the relative safety of one alternative over the other. Rather, alternatives were compared to the study chemical as a baseline. This report provides information in the three assessment areas for each alternative and invites readers to use and supplement this material as appropriate for the specific considerations and requirements that they face. Users should use the material presented here for guidance in conducting their own assessments, taking into account the values, priorities, and situation-specific requirements that are most relevant for their organizational, industrial, or policy goals.

Economic Impact Assessment

In addition to collecting financial information as part of each alternatives assessment, the Institute convened a group of economists and other experts to discuss broader economic patterns, including the possible impacts on employment and competitiveness from adopting alternatives in Massachusetts.

Lead and Lead Compounds

Lead is a naturally occurring metal with a high density and low melting point. It is ubiquitous in manufactured products in many forms: as a pure metal, as an alloy with other metals, and in compounds. It is valued for its electrical conductivity, high density, and ability to stabilize plastics.

Lead poses a serious threat to human health and the environment. Acute human health effects of high lead exposures can include gastrointestinal distress, brain and kidney damage, and death. Chronic effects of lead exposure include anemia, damage to the nervous system, effects on blood pressure and kidney function, and interference with vitamin D metabolism. The U.S. Environmental Protection Agency (EPA) has classified lead as a probable human carcinogen, and the International Agency for Research on Cancer (IARC) has classified inorganic lead as probably carcinogenic to humans (Group 2A). Fetuses, infants and children are particularly vulnerable to adverse effects from lead exposure, including irreversible neurological damage. There is no known safe threshold for lead exposure in children.

Lead is extremely persistent in both water and soil. Combustion of leaded gasoline was a major source of anthropogenic lead releases in the past. Industrial releases from smelters, battery plants, chemical plants, and disturbance of older structures containing lead based paints are now major contributors to total lead releases.

The Institute selected three priority uses of lead to assess in detail: ammunition, weighting applications, and heat stabilizers for PVC wire and cable coatings. These applications were chosen based on stakeholder interest, importance to Massachusetts industry and consumers, and likely availability of alternatives. Ammunition used at indoor and outdoor firing ranges is a significant source of occupational lead exposure and environmental contamination. Automotive wheel weights and fishing sinkers were chosen as representative of a large number of lead uses that rely on its high density. Wire and cable heat stabilization is the category with the largest use of lead among Massachusetts manufacturers. The results of these assessments are summarized below.

Ammunition for shooting ranges

Most practice shooting ranges currently use lead ammunition. Range operators and shooters can be exposed to high airborne lead levels in indoor shooting ranges. Use of lead ammunition at outdoor shooting ranges can produce environmental contamination.

Most of the major ammunition manufacturers now market lead-free bullets. A few smaller ammunition manufacturers specialize in the production of lead-free ammunition.

The Institute examined five possible alternatives to lead ammunition for use in shooting ranges: bismuth, copper, iron, tungsten, and zinc. For each alternative, the Institute examined human health, environmental, technical, and cost criteria.

- **Human health.** The alternative materials are all superior to lead from a human health perspective for the criteria the Institute considered (carcinogenicity, developmental toxicity, and occupational exposure).
- **Environment.** In general, the alternatives are more desirable from an environmental standpoint, with the exception of aquatic toxicity for copper and zinc.
- **Technical criteria.** Technical criteria of interest for this application include density, frangibility, and barrel wear.
    - Greater bullet density is advantageous for most ammunition applications, since high bullet weight and small bullet size are both desired characteristics. Tungsten has greater density than lead, while the other alternatives have lower density than lead. However, the density of bismuth is very close to that of lead. One manufacturer produces bismuth bullets that match the weight of many lead bullets.
    - Many lead-free bullets are frangible, which means they fragment into small particles upon impact with a target. Frangible bullets are safer than lead bullets for use at indoor firing ranges because they reduce or eliminate the dangers associated with ricocheting bullet fragments. This is of particular concern when firing at steel targets at close range. Frangible bullets can also limit damage to steel targets. Bismuth, iron, tungsten/nylon, and powdered copper can all be used to make frangible bullets. Solid copper bullets are not frangible and may ricochet more readily than lead bullets. Some zinc bullets break apart upon entering a target, but their probability of ricochet is not known.
    - Barrel wear is the erosion of barrel material by bullets. All of the alternative materials except tungsten are similar to lead from the perspective of barrel wear.
- **Cost.** All the alternatives currently have a higher purchase price than lead bullets. However, all the alternatives are superior to lead bullets from the perspective of operating costs. Firing ranges face numerous costs associated with the use of lead ammunition. These can include costs of air monitoring, blood lead level testing of range operators, maintenance of containment and filtration systems, purchase of replacement filters, range cleaning, and lead

disposal. By switching to lead-free ammunition, firing ranges can reduce or eliminate costs in these areas. In addition, lead bullets and bullet fragments must be either recycled or disposed of as hazardous waste. Alternative bullets, in contrast, can be disposed of as non-hazardous waste if they are not recycled. Frangible bullets also reduce wear and damage on bullet traps and backstops.

Weighting applications

The Institute chose wheel weights and fishing tackle as two examples of the larger category of lead used in weighting applications.

Fishing sinkers

Nearly 2,500 metric tons of lead are used each year in the United States to produce fishing sinkers. Many of these sinkers are lost during use. One study found that anglers lost, on average, one sinker every six hours of fishing.

Lead sinkers are lethal to waterbirds, such as loons and swans. One study found that the most common cause of death in adult breeding loons was lead toxicity from ingested fishing sinkers.

A number of states have placed limits on the use of lead fishing sinkers. In Massachusetts, lead sinkers are prohibited for use in the Quabbin and Wachusett Reservoirs, the two bodies of water that support the core of the state's loon population. Use of lead sinkers is restricted in several other states in the Northeast, and is restricted or banned in several countries.

Many anglers produce their own lead sinkers at home. This activity can expose individuals and family members to airborne lead particles or vapors.

The Institute examined five possible alternatives to lead for use in fishing sinkers: bismuth, ceramic, steel, tin, and tungsten. For each alternative, the Institute examined human health, environmental, technical/performance, and cost criteria.

- **Human health.** All the alternative materials are superior to lead from the perspective of the human health criteria the Institute examined (carcinogenicity, developmental toxicity, and occupational exposure).
- **Environment.** The alternatives are generally superior to lead from an environmental standpoint as well. All of the alternatives are clearly less hazardous to waterfowl and other aquatic species than lead.
- **Technical criteria.** The principal technical criteria of interest for this application are density, hardness, malleability, melting point, and corrosion resistance.
  - Tungsten is more dense than lead; all the other alternatives are less dense than lead.
  - Harder materials are preferable for use in many sinkers. All the alternatives are harder than lead; pure tin is about equal to lead in hardness, while tin alloy is harder than lead.
  - Greater malleability is an advantage for sinker applications where the sinker is crimped on to the fishing line. Tin has malleability equal to that of lead; all of the other alternatives are less malleable than lead.
  - Low melting point is considered an advantage because it allows individuals to produce sinkers at home, although home production of lead sinkers also creates

    human health hazards. Bismuth and tin have lower melting points than lead; ceramic, steel, and tungsten have higher melting points.

  - Carbon steel is less resistant to corrosion than lead. Stainless steel and all the other alternatives are similar to lead in this regard.

- **Cost.** The alternatives generally have a higher retail price than lead sinkers, although some steel sinkers are competitive in price with lead sinkers. Studies conducted in the 1990s suggested that fishing sinker purchases represent less than 1% of total expenditures by anglers on their sport, so an increase in fishing sinker costs would be unlikely to have a significant effect on users.

Wheel weights

Wheel weights often fall off automobile wheels, leading to lead contamination of the environment. Worker exposure is a concern in the installation of wheel weights.

There is a thriving market in lead-free wheel weights. European and Japanese automobile manufacturers have already switched to lead-free wheel weights and U.S. automobile manufacturers are currently in the process of making the switch. Asian auto manufacturers now primarily use steel weights. Zinc weights are used widely in Europe, and US auto manufacturers are using zinc weights for automobiles destined for export to Europe. General Motors and Ford are in the process of converting to steel weights.

Despite these developments, the U.S. market in replacement wheel weights continues to use lead weights almost exclusively. This market in replacement weights accounts for 80% of total wheel weight use in the U.S.

The Institute examined four possible alternatives to lead wheel weights: copper, steel, tin, and zinc. For each alternative, the Institute examined human health, environmental, technical/performance, and cost criteria.

- **Human health.** All of the alternative materials are superior to lead for the human health criteria the Institute examined (carcinogenicity, developmental toxicity, and occupational exposure).
- **Environment.** For the most part the alternatives are superior environmentally, although zinc is inferior for aquatic toxicity in salt water, and copper is inferior for aquatic toxicity in both fresh and salt water.
- **Technical criteria.** The principal technical criteria of interest for this application are density, malleability, and corrosion resistance.
  - All of the materials considered in this analysis are less dense than lead. Thus, in order to achieve the same mass, the weights made from alternative materials must be somewhat larger than their lead counterparts. This adjustment does not typically pose engineering difficulties for weights used on passenger vehicles.
  - The malleability of lead makes it possible to shape wheel weights to match the curve of the wheel diameter. The malleability of copper and tin is similar to that of lead; steel and zinc are less malleable. Manufacturers can compensate for lower malleability by creating segmented weights.

  - The corrosion resistance of the alternative materials is generally similar to that of lead; tin is superior to lead in this regard because it does not require coating.
- **Cost.** Copper and tin weights are expected to cost more than lead weights at initial purchase; zinc weights cost about the same as lead weights, and steel weights have equal or lower cost. The end of life costs for all the alternatives are lower than those for lead.

Heat stabilizers for PVC wire and cable coatings

Lead heat stabilizers used for polyvinyl chloride (PVC) constitute the largest use of lead compounds in Massachusetts manufacturing, and the wire and cable industry is the largest user of these compounded resins.

Significant progress has been made in the identification and adoption of alternatives. Many lead-free heat stabilizers are commercially available, and resin compounders are working proactively with wire and cable companies to encourage their adoption. Regulatory requirements prohibiting the use of lead and other hazardous substances in electrical and electronic equipment in the European Union have created an incentive for U.S. manufacturers to develop lead-free alternatives. The Institute is engaged in on-going collaborative projects to help Massachusetts industries to gain and maintain a competitive edge in producing lead-free wire and cable, as well as lead-free electrical and electronic equipment.

The Institute did not conduct a complete technical assessment for alternative heat stabilizers. Each application has unique technical requirements, and stabilizers are formulated with many different combinations of chemicals to suit each application. Furthermore, heat stabilizers will be examined as part of a collaborative project between the Institute and the U.S. EPA to conduct a detailed life cycle assessment for three specific wire and cable applications. However, many Massachusetts wire and cable companies plan to adopt lead-free alternatives before that study will be complete. Thus, stakeholders determined that it would be useful for the Institute to analyze the environmental health and safety profiles of chemicals that are widely used in alternative stabilizers.

The Institute gathered information on five categories of alternative heat stabilizers: calcium-zinc, barium-zinc, magnesium-zinc, magnesium aluminum hydroxide carbonate hydrate, and magnesium zinc aluminum hydroxide carbonate. From these categories, the Institute selected five representative heat stabilizer products and conducted an environmental health and safety assessment of their constituent materials. Many of these constituent materials were found to be superior to lead from a human health and environmental perspective. Costs of mixed metal heat stabilizers have decreased in recent years, such that a transition to a mixed metal heat stabilizer may be cost neutral. Where a cost differential exists, it is estimated at 10% or less.

Formaldehyde

Formaldehyde is a naturally occurring chemical found in small quantities in the human body. Products that are made from or contain formaldehyde include many resins, permanent press fabric treatments, lawn fertilizers, cosmetics and disinfectants. Wood adhesives used to make plywood, particleboard and other manufactured wood products are the dominant end use for this chemical. The plastics industry also uses formaldehyde-based resins extensively. Formaldehyde is also used as a sterilant and tissue preservative. It is used to preserve animal specimens used in secondary school and college biology classes. It is also used to preserve human and animal tissue in medical and scientific laboratory settings. Embalmers use formaldehyde to preserve human remains for burial.

Formaldehyde exposure through consumer products or industrial activity is very hazardous to human health. Formaldehyde is highly irritating, acts as a potent sensitizer, and is known to cause cancer in humans. In 2004 IARC moved formaldehyde from Group 2A (probable human carcinogen) to Group 1 (known human carcinogen). Ingestion of formaldehyde or exposure to very high air concentrations can cause death.

The Institute assessed alternatives to formaldehyde in three categories of use: sanitary storage in barbering and cosmetology, preserved educational specimens for dissection, and building panels.

Sanitary storage in barbering and cosmetology

The Massachusetts Board of Cosmetology requires cosmetology salons to use dry sanitizer made from paraformaldehyde (a polymerized solid form of formaldehyde) in drawers where instruments are stored. The perforated plastic containers containing para-formaldehyde emit formaldehyde as it de-polymerizes into formaldehyde gas, filling the cabinets and drawers where hair brushes are kept, and subsequently entering the salon and classroom air as drawers are opened. Use of this dry sanitizer has placed a consistent source of formaldehyde in salons and cosmetology training schools, including vocational high schools.

The Institute identified and evaluated two possible alternatives to the use of dry sanitizer in drawers. The first option is a process change: storage of implements in a disinfected, dry, covered container or drawer without the use of any additional sterilant. The second option is to use ultraviolet (UV) light cabinets for sanitary storage.

The Massachusetts Board of Cosmetology is the only such board in the U.S. that requires use of dry sterilants. In contrast, the National-Interstate Council of State Boards of Cosmetology (NIC) does not recommend use of formaldehyde-based dry sterilants due to their carcinogenic potential. In place of dry sterilants, the NIC recommends an alternative procedure of proper cleaning, wet disinfection, drying and storage. The disinfection and storage practices recommended by the NIC are reiterated in the rules of many other Boards of Cosmetology and in the field's primary textbook and practice guidance.

Process change

One practical alternative to use of dry sterilant is simply to store implements in a disinfected, dry, covered container that is isolated from contaminants. This option would produce cost savings, because it would eliminate the need for cosmetology salons to purchase dry sterilant.

Simple elimination of dry sterilant, without any other change in procedures, is superior to use of dry sterilant from the human health, environmental, and cost perspectives. It is equivalent from a technical perspective.

UV light cabinets

Another option is for cosmetology salons to use UV light cabinets. A disadvantage of this technology is that although UV germicidal light is effective at killing pathogens, it must strike all surfaces and this is difficult to achieve on a brush. The cabinets may also become reservoirs of pathogens if they are not regularly cleaned and disinfected.

Use of UV storage cabinets is superior to use of dry sterilant from a human health and environmental perspective, although there is the potential for UV light exposure if the cabinets are misused. This system has a higher cost than dry sterilant.

Preserved educational specimens for dissection

Secondary school and college students in anatomy classes dissect preserved specimens, including fetal pigs, frogs, cats, sharks and other species. Traditionally, educational specimens have been preserved with a formalin solution (a 37% solution of formaldehyde in water). Formaldehyde kills the bacteria that would otherwise decay the tissue. It also polymerizes the tissue, helping to maintain its texture, structure and color. This application does not account for a large percentage of formaldehyde use, but it poses particular public exposure concerns. Students, laboratory instructors and technicians are exposed to formaldehyde through their repeated contact with these specimens.

The Institute evaluated two categories of alternatives: use of specimens that are formaldehyde-free, and the technological alternative of video and virtual dissection.

Specimens in alternative solution

Using specimens of grass frogs as a typical application, an outside expert evaluated the technical performance of three alternative preservatives: Formalternate by Flinn Scientific, Wardsafe by Ward Scientific, and Streck Tissue Fixative (S.T.F.) Preservative by Nebraska Scientific. Formalternate is a combination of propylene glycol, ethylene glycol phenyl ether and phenol. Wardsafe is primarily glutaraldehyde. S.T.F. is a mixture of diazolidinyl urea, 2-bromo-2-nitropropane-1, 3-diol (Bronopol), zinc sulfate, and sodium citrate. Different species may be preserved in different solutions by the same company. All these alternative products are readily available from well-established companies.

- **Health.** All three alternatives are superior to formaldehyde-containing specimens from the perspective of carcinogenicity, sensitizing potential, and capacity to cause irritation. Some ingredients of the alternatives can cause skin, eye and respiratory irritation, and some can act as sensitizers, but they are less hazardous than formaldehyde on all these measures. Evaluating the health effects of Formalternate and S.T.F. is complicated by the fact that they are chemical mixtures. Glutaraldehyde, used in Wardsafe, has high acute toxicity, but is present at low concentrations in the specimen.
- **Environment.** Some of the chemicals used in the alternative fixatives are more toxic to fish and other species than is formaldehyde. In general, the low volatility and small amounts of preservative in the alternative specimens suggests that exposure for humans and the environment are likely to be very low. Life cycle considerations for the alternatives include the use and disposal of some ingredients, such as phenol and zinc sulfate, which are potential environmental pollutants.
- **Technical criteria.** All of alternatives match or exceed the important technical and performance criteria for educational specimens: color, texture, and stiffness of the specimen

tissue. The color of the alternative specimens was as good as or better than the formalin-preserved specimen. The specimens varied in texture but all had acceptable characteristics.

- **Cost.** The prices of alternative specimens are similar to each other and generally less expensive than the formalin-fixed specimen.

Process change: Video dissection

Another alternative is to use video/virtual dissection instead of physical dissection of a preserved specimen.

- **Health and Environment.** Video/virtual dissection does not pose any of the health or environmental hazards for students or instructors associated with dissection of preserved specimens.
- **Technical criteria.** Video/virtual dissection offers different pedagogic opportunities from those afforded by physical dissection. Some instructors believe that video dissection is not an adequate substitute for dissection of preserved specimens, although it may be a useful supplement. However, the educational utility of video and/or virtual dissection may vary with the class or instructor. A complete assessment of the educational benefits of each option was beyond the scope of this study.
- **Cost.** The cost of video/virtual dissection programs is variable. Low or no-cost materials are available, as are more expensive programs. In contrast to preserved specimens, these represent a one-time cost.

Hardwood plywood and structural use building panels

Adhesives used to make plywood, particleboard and other manufactured wood products account for the majority of formaldehyde consumed world wide each year. The components of wood panels vary depending on their intended use. Plywood and other products that are "exterior-grade" or need to withstand wet conditions are usually made with phenol-formaldehyde resin. Particleboard and medium density fiberboard, often used for making furniture and cabinetry, are made with less expensive urea-formaldehyde resins, which have higher levels of formaldehyde emissions. Melamine-formaldehyde resins and polyacetal resins are also used in wood products and laminates and in molded plastic parts.

The Institute examined three alternatives that are currently available: Columbia Forest Products soy-based resin hardwood plywood panels, Homasote's recycled paper panel boards, and Viroc's wood fiber Portland cement panels. The Institute also assessed one emerging alternative that is not yet on the market, JER EnviroTech's plastic-wood fiber panel.

Hardwood plywood

The Columbia Forest Products soy-based resin hardwood plywood panel (Purebond) is a hardwood veneer core plywood panel. It can be used to make cabinets, built-in furniture, paneling, shelving, doors and other uses requiring a high end wood product.

- **Human health.** Purebond is superior to formaldehyde-resin plywood from the perspective of carcinogenicity and irritation/sensitizing properties. It eliminates potential formaldehyde exposures for users. However, its production involves use of epichlorohydrin as an intermediate. Epichlorohydrin is classified as a probable human carcinogen and poses other hazards to human health and the environment. This chemical could be a hazard to workers and the environment during production.

- **Environment.** The formaldehyde-based resin in conventional plywood has minor ecotoxicity. Purebond is similar to formaldehyde-resin plywood for this parameter.
- **Technical Criteria.** Technical characteristics of interest for this application include appearance/construction, strength of the glue bond when moist, fire resistance, warp resistance, and product availability. Purebond is similar to formaldehyde-containing plywood for the parameters of appearance/construction, fire resistance, and product availability. It has a glue bond superior to that of urea-formaldehyde plywood under conditions of moisture. Its warp resistance has not been assessed fully.
- **Cost.** Purebond is currently available at a similar cost to formaldehyde-resin plywood.

Structural use panels

The Institute assessed two alternatives that could be used in place of softwood plywood for structural use panels: Homasote's recycled paper panel boards, and Viroc's wood fiber Portland cement panels.

Homasote's recycled paper panels and Viroc's wood fiber Portland cement panels may be used in place of softwood plywood and oriented strand board (OSB) in exterior sheathing, roof decking and floor decking. Viroc is used extensively in Europe.

- **Health.** Viroc and Homasote do not present a hazard to building occupants, but there are some occupational exposure concerns, such as exposure to wood and cement dust during cutting. Both products are superior to formaldehyde-resin plywood from the perspective of carcinogenicity of the binder. The Homasote panels are superior from the perspective of irritant in binder, while the Viroc panels are similar to formaldehyde-resin plywood on this metric.
- **Environment.** Both products are superior to formaldehyde-resin plywood from the perspective of ecotoxicity and natural resource conservation. The Viroc product is inferior from an energy intensity life cycle perspective**.**
- **Technical criteria.** Technical and performance criteria of interest for these uses include strength, weight, response to moisture, storage, handling, fastening, finishing, fire resistance, thermal resistance, and mold, rot and insect resistance. Both alternatives present some advantages and some disadvantages on these metrics. For example, Homasote is superior to formaldehyde-resin panels on several measures including resistance to insects, rot, and mold, and is inferior on certain other measures, such as impact resistance and tensile strength. Viroc is superior on measures including resistance to insects, rot, and mold, fire resistance, and impact resistance, and inferior on parameters such as tensile strength. Both Viroc and Homosote panels must be thicker and heavier than formaldehyde-resin panels to withstand an equivalent load over the same span.
- **Cost.** Both alternatives are currently more expensive than traditional formaldehyde-containing plywood.

Emerging alternative

The JER Envirotech Company is in the process of developing an extruded building panel made of wood fiber and polypropylene thermoplastic. This is an "emerging technology" that may substitute for particleboard and structural uses. The Institute did not assess this alternative in detail, but encourages further study of this option.

Perchloroethylene

Perchloroethylene (PCE) is a synthetic chlorinated hydrocarbon. It is used primarily as a solvent in dry cleaning and industrial degreasing and as a chemical intermediate.

Short-term exposure to PCE can cause symptoms such as skin, eye, and respiratory irritation, headache, and nausea; very high exposure can be fatal. Long term exposure to PCE may cause liver, kidney or central nervous system damage. PCE may also affect the developing fetus. IARC lists PCE as a probable human carcinogen (Group 2A).

PCE most often enters the environment through fugitive emissions from dry cleaning and metal degreasing industries and by spills or accidental releases to air, soil or water. Exposure results from environmental contamination, presence in consumer products or occupational sources. PCE has been found in breast milk, one indication of its ubiquitous presence in the environment.

The Institute assessed alternatives to PCE in three categories of use: dry cleaning, vapor degreasing, and aerosol automotive cleaning.

Dry cleaning

The Institute analyzed five categories of PCE alternatives for dry cleaning: hydrocarbons (HC), volatile methyl siloxanes (VMS), substituted aliphatic glycol ethers (SGE), wet cleaning, and liquid carbon dioxide (CO_2). Like PCE, the first three of these categories are based on organic solvents. For each category except CO_2, the Institute selected an individual chemical or process as a representative of the broader category.

- **Health.** All the alternatives are superior to PCE from the perspective of carcinogenicity. VMS and CO_2 are superior from the perspective of irritation, while SGE and wet cleaning are roughly equivalent to PCE on this metric. HC, wet cleaning, and CO_2 are superior from the perspective of exposure limits. Recent research has raised concerns about adverse effects of decamethylcyclopentasiloxane (D5), the dry cleaning solvent used in the VMS system, in laboratory animals.
- **Other hazards.** Unlike PCE, HC and VMS are combustible.
- **Environment.** The alternatives are less persistent than PCE in water, soil, sediment, and air, with some exceptions: the hydrocarbon alternative is more persistent than PCE in soil. The CO_2 used in the process is captured from industrial processes and thus the garment cleaning adds no net CO_2 to the atmosphere.
- **Technical criteria.** The first four alternatives are commercially available in Massachusetts. No commercial CO_2 facilities were identified in Massachusetts, although there are facilities in other states. Thus, all of the alternatives are known to have commercial viability at this time. Technical criteria of interest for this application include time for washing; load capacity; the range of soils that can be removed effectively; the types of clothing that can be washed using a given system; and the efficiency of spot cleaning before washing.

  - All the alternatives require more time for cleaning than PCE, except CO_2, which requires less time. This time differential is decreasing as operators gain more experience with the alternatives. The alternatives are variable on the metric of load capacity: VMS is superior on this metric and wet cleaning is superior in some cases, while carbon dioxide is similar to PCE and HC and SGE are inferior.
  - The hydrocarbon and VMS alternatives are able to clean fewer types of soil compared with PCE. The SGE and carbon dioxide systems are similar to PCE on this metric. Wet cleaning can be either equivalent or inferior to PCE on this metric.
  - HG and SGE are superior to PCE in the range of types of clothing that they can clean. VMS is similar to PCE on this metric, and wet cleaning and carbon dioxide are more limited in the range of clothing types they can clean.
  - Carbon dioxide is superior on the spotting metric; hydrocarbon, VMS and wet cleaning are inferior; and SGE can be either similar or inferior to PCE on this metric.
- **Cost.** Cleaning system costs include equipment, solvent, labor, energy, and regulatory costs. The Institute gathered comparative cost information on these parameters from a number of Massachusetts cleaners. Hydrocarbon systems have higher equipment and labor costs, counterbalanced by lower solvent and regulatory costs. VMS systems have higher equipment cost; figures were unavailable for several other parameters. SGE systems have higher equipment and solvent costs, counterbalanced by lower regulatory costs. Wet cleaning has higher labor costs, counterbalanced by lower equipment, solvent, and regulatory costs. Carbon dioxide has higher equipment costs and lower regulatory costs.

Vapor degreasing

The Institute carried out alternatives assessments on one product based on n-propyl bromide (nPB), a product based on a volatile methyl siloxane (VMS), and two hydrochlorofluorocarbons (HCFCs). All of these are solvent-based vapor degreasing substitutes for PCE. The Institute did not conduct an alternatives assessment on aqueous cleaning systems as part of this project because the Institute's Surface Solutions Laboratory has already produced extensive resources in this area. As documented in other work by the Institute, approaches other than use of a drop-in solvent replacement are often superior from a health, environmental, technical and cost perspective.

- **Health.** All of the alternatives have potentially significant environmental and occupational health and safety impacts. The HCFC products have significant adverse environmental impacts, including persistence and global warming potential, but should be somewhat less toxic than PCE. There are significant concerns about the toxicity of nPB; it is a neurotoxin, and its carcinogenicity is now under study. Exposure to high levels of VMSs can cause dizziness, disorientation, and shortness of breath.
- **Other hazards.** All of the alternatives have higher vapor pressures than PCE, which will lead to greater evaporation and the potential for more vapors to escape from the degreaser; this will increase the potential for worker exposure, and may cause greater fugitive emissions than with PCE. A significant safety hazard is presented by the VMS product, which is highly flammable with a very low flash point. Its use as a vapor degreaser would present a significant fire and explosion hazard, and special handling would be required to use it safely, including the requirement for a closed system, spark-proof equipment, and worker training.

- **Environment.** nPB and VMS are superior to PCE on measures of persistence in water, soil, sediment, and air. The two HFCs are inferior on these measures. nPB is superior from the perspective of bioaccumulation, while the others are inferior on this measure. The two HFCs also have global warming potential.
- **Technical criteria.** Over all, the vapor degreasing alternatives have technical features comparable to those of PCE. The alternatives all have higher vapor pressures than PCE, which will contribute to product loss through evaporation. On the other hand, the alternatives all have lower surface tensions than PCE, which should enhance their ability to clean complex parts. Soil removal testing performed at the Institute's Surface Solutions Laboratory found that all four alternatives were as effective as PCE in removing oil-based soils.
- **Cost.** All the alternatives currently cost more to purchase than PCE, creating an initial barrier for companies interested in switching to an alternative vapor degreaser. Operating costs such as energy use, waste solvent handling costs, and solvent lifetime may help to offset this higher purchase price. For example, many of the alternatives can be used at lower operating temperatures than PCE to achieve the same level of cleaning performance. On the other hand, all of the alternative solvents are more volatile than PCE, which might increase costs due to greater evaporative losses.

When addressing a specific cleaning need it is important to consider all options, including process and product modifications. Therefore, other options to consider include alternative cleaning processes such as an aqueous or a semi-aqueous system, working within the supply chain to change the contaminant on the part that requires cleaning, or investigating a material change to prevent contamination and thereby making cleaning unnecessary. All of these options would be preferable to using PCE or any of the drop-in alternatives discussed here. The Institute has demonstrated the viability of this approach in projects to assist industry in replacing chlorinated solvents with safer alternatives.

Aerosol automotive cleaning

The Institute carried out alternatives assessments on four brake cleaning alternatives, seven external engine cleaning alternatives, three internal engine cleaning alternatives, and four tire cleaning alternatives.

- **Health.** With regard to human toxicity, products containing n-hexane, 2-butoxyethanol, DGME, toluene, and glycol ethers are of equal or more concern compared with products containing PCE. Aqueous-based products will have lower human health concerns than any of the solvent-based products.
- **Other hazards.** Most of the solvent-based cleaners are highly flammable, and great care must be taken in their use, especially around hot engines. PCE is nonflammable, as are the aqueous-based cleaners, so these alternatives are preferable with regard to fire potential.
- **Environment.** Many of the alternative cleaners have the potential for significant environmental impact upon release. The medium of most concern is air, since these products are used as aerosol sprays. Most of the alternative products have ingredients with atmospheric half-lives exceeding two days and thus, like PCE, are considered persistent.

- **Technical criteria.** It is difficult to assess the technical performance of the alternatives objectively, since test data are not available. Stakeholders indicated that the alternative solvent-based cleaners are likely to perform as well as PCE-based cleaners, while aqueous-based cleaners may require more mechanical agitation to achieve equivalent results.
- **Cost.** Cost information is also difficult to assess. Some alternative products were more expensive per ounce than the corresponding PCE product, and some were less expensive per ounce. The actual cost per use may be quite different, however, since more or less of the different products may be required to obtain equivalent levels of cleaning.

Hexavalent Chromium

Chromium is a metallic element found in nature in the form of chromite ore or the mineral crocoite. Chromium provides manufactured products with hardness, shininess, durability, color, corrosion resistance, heat resistance, and decay resistance. Important uses of chromium compounds include wood preservation, metal processing, leather tanning, and production of pigments. The major application of chromium is in the production of alloys, primarily stainless steel; historically, this has amounted to 50-60% of total chromium use.

There are several oxidation states of chromium, each with its own chemical characteristics. The most common forms are trivalent chromium and hexavalent chromium. Trivalent chromium compounds occur naturally, while the hexavalent compounds result primarily from industrial activity.

Hexavalent chromium poses far more health hazards than trivalent chromium. Short-term effects of hexavalent chromium exposure can include eye and respiratory irritation and sensitization. In large quantities, ingestion of hexavalent chromium compounds can result in acute gastroenteritis, vertigo, gastrointestinal hemorrhage, convulsions, ulcers, kidney damage or failure, and liver damage or failure. Acute skin exposure can cause burns, liver damage or failure, kidney damage or failure, and anemia. Effects of chronic skin exposure include dermatitis, hypersensitivity reactions, eczema, and kidney or liver damage. Hexavalent chromium is classified by IARC as a known human carcinogen (Group 1).

Workers have the highest risk of adverse health effects from hexavalent chromium exposure. The industries with the greatest risk of occupational exposure are chrome electroplating, stainless steel welding, metal coating and painting, printing, textiles, leather tanning, wood preservation, and cement or masonry work.

The Institute assessed three general categories of use: decorative chrome electroplating; hard chrome electroplating; and chromate conversion coatings. The category of chromate conversion coatings was narrowed further to focus only on passivation of zinc and zinc alloy plated parts and zinc galvanized steel.

Decorative chromium electroplating of consumer and automotive products

Decorative chrome plating is used for consumer applications such as appliances, metal furniture, plumbing fixtures, knobs and hand tools, and for automotive trim. It creates an attractive blue-white finish and helps to reduce tarnishing.

The major advantage of decorative hexavalent chromium is its appearance, especially its blue-white color. It also presents some processing difficulties. These include poor throwing power (a measure of coverage in recessed areas of a part being plated), low resistance to burning during plating, difficulty in removing impurities from the plating bath, problems in rinsing the plating solution from the plated parts, and intolerance to interruptions or variations in the electrical current during plating.

The Institute assessed two alternatives to hexavalent chromium for decorative chrome electroplating: trivalent chromium plating baths, and low temperature arc vapor deposition of trivalent chromium.

- **Trivalent chromium plating baths** use a very similar process to that used in hexavalent plating.
- **Low Temperature Arc Vapor Deposition (LTAVD®)** is a proprietary process in which parts to be coated are exposed to a vaporized metal that condenses on the parts, depositing a thin, solid film.

The Institute assessed health, environmental, technical, and cost criteria for each of these alternatives.

- **Health.** Both options are superior to hexavalent chromium plating from the perspective of carcinogenicity and occupational exposure standards. LTAVD® is superior from the perspective of skin irritation/sensitization, and trivalent chromium baths are either similar or superior to hexavalent chromium baths on this metric.
- **Environment.** Both options are superior to hexavalent chromium plating from the perspective of waste generation. LTAVD® avoids the need for a lead anode; trivalent chromium baths may or may not use a lead anode.
- **Technical criteria.** Criteria of interest include uniformity of coating, adhesion to substrate, hardness, color, and resistance to corrosion and wear.
    - Decorative trivalent chromium plating has many processing advantages over hexavalent chromium plating. Examples of these advantages include superior throwing and covering power; tolerance of electrical current interruptions; low susceptibility to burning; and ease of rinsing and removing impurities. Trivalent chromium plating has a naturally micro-porous structure, which is advantageous for corrosion resistance. In the past, the color of trivalent chromium plating was a disadvantage, but recent developments now make it possible to produce a trivalent plate with an appearance equivalent to that produced using hexavalent chromium.
    - LTAVD® operates at room temperature, making it possible to use it on a substrate with a low melting point, such as plastic. By using different combinations of gases and metals, a variety of coatings can be formed. Metals with dissimilar characteristics, such as titanium and aluminum, can be alloyed using this process, creating unique coating materials. Most of the technical assessments of LTAVD® have been conducted by the company that holds the patent rights. Findings of these assessments indicate that LTAVD® produces a very uniform coating with good adhesion to the substrate, corrosion resistance similar to or better than that of hexavalent chromium, color similar to that produced with hexavalent chromium, and hardness superior to that produced with hexavalent chromium.
- **Cost.** Trivalent plating chemicals are more expensive than hexavalent plating chemicals, although economies of scale are likely to lead to falling prices as trivalent systems increase in popularity. The cost of chemicals, however, is offset by the greater efficiency of the trivalent

process and greatly reduced costs for exposure control and disposal. One study estimated that the volume of sludge generated by the hexavalent process is about 30 times that of the trivalent process. Another found that hexavalent treatment costs were nearly 10 times that of the trivalent process. While cost information for LTAVD® has not been published, the process is being used by several major manufacturers of consumer hardware, indicating that it is commercially viable. Since a wide variety of gases and metals are used, material costs also would vary accordingly. A major operating cost would be energy. Waste treatment costs are likely to be minimal.

Hard chromium electroplating of industrial components

Hard chrome plating, also known as functional or industrial chrome, typically is thicker than decorative chrome. It is used on industrial components that must perform under demanding conditions such as high temperatures, and repetitive grinding and impact forces (such as aircraft engines and landing gear, hydraulic cylinders, and drill bits). Unlike decorative chrome, appearance usually is not an important issue.

The two main reasons for using hard chrome are to provide wear and corrosion resistance, and to rebuild worn components to precise dimensions. It has a low coefficient of friction, is hard and heat-resistant, adheres well to substrates of various geometries, and provides corrosion resistance.

Hard chrome plating suffers from a number of technical limitations. The plating process involves numerous steps, which may need to be repeated in order to achieve an adequate coating. The coating can be brittle, leading to failure or reduced corrosion resistance. It can also be difficult to achieve even plating thickness.

The Institute assessed six processes that can serve as alternatives to hard chromium electroplating:

- **Thermal sprays** include high velocity oxy-fuel (HVOF) and plasma sprays. Thermal spray is a coating process in which wire or metallic powder is melted by a high temperature flame and sprayed as particles or droplets onto a substrate.
- **Weld facing** is a dry method of joining a hard coating, edge, or point to a metal or alloy substrate to improve its resistance to abrasion, corrosion, heat or impact. It also is used to restore worn surfaces.
- **Heat treatments and plasma nitriding** methods use heat to diffuse elements into the top surface of a substrate metal to form an alloy or layer with desired properties.
- **Nanocrystalline coatings** use electrodeposition, vapor deposition, or spray conversion processing to deposit very small grains of crystalline alloys on a metal substrate.
- **Vapor deposition:** In *physical vapor deposition (PVD)***,** parts to be coated are exposed to a vaporized metal that condenses on the parts, depositing a thin, solid film. Types of PVD processes include ion plating, vacuum evaporation, thermal evaporation, electron beam evaporation, and sputter deposition. *Chemical vapor deposition (CVD)* is similar to PVD, but uses gases that combine on a hot surface to form the hard coating.
- **Functional trivalent plating**: The Faraday Technologies' Faradaic™ process is similar to the wet hexavalent plating process, with the capability to plate a thick, functional chromium coating using a trivalent chromium plating bath. It is intended as a "drop-in" alternative to hexavalent baths.

Some of these categories include several related processes that differ in their functional details. In addition, the categories often overlap to a certain extent, so that a given process may be classified differently in different sources. Surface coatings of various materials, typically other metals, alloys, and metal carbides or nitrides, can be applied using these processes. Coatings that may be used to replace hard chrome include those based on titanium, tungsten, cobalt, aluminum and silicon.

For each of these alternatives, the Institute assessed human health, environmental, technical, and cost criteria.

- **Health.** All the alternatives are superior to hexavalent chromium from the perspective of carcinogenicity. However, there are health hazards associated with the alternatives as well. For example, thermal sprays may contain cobalt powder, which is classified as possibly carcinogenic to humans. This is an improvement over hexavalent chromium, which is classified as a known human carcinogen.
- **Environment.** All the alternatives are superior to hexavalent chromium from the perspective of waste generation.
- **Technical criteria.** All of the alternatives have the potential to offer equivalent or better performance compared to hard chrome plating, although several have some limitations in their application. However, given the range of alternative processes and coating materials, there is likely to be at least one alternative that can meet the technical requirements of every hard chrome plating application.
- **Cost.** Many of the alternatives require a significant capital investment. On the other hand, the manufacturers of these systems claim that operating costs are significantly reduced. In some cases, new equipment may pay for itself within a few years through reduced operating costs.

Passivation of zinc plated parts and zinc galvanized steel

Passivation is a surface treatment that provides resistance to corrosion. The protection is afforded by a film or thin coating that interacts with the underlying metal. Hexavalent chromium is a standard passivating chemical for zinc and zinc-alloy plated parts, and zinc galvanized steel.

In passivation with hexavalent chromium, zinc plated parts are dipped into an acidic solution containing a mix of chemicals. The solution reacts with the plating to form a film of zinc chromate and other chromate compounds in both the trivalent and hexavalent state. This is referred to as a "conversion coating" because the hexavalent chromium solution converts the surface to zinc chromate. The hexavalent chromium reacts with the metal, forming an inert trivalent chromium layer with "releasable" hexavalent chromium ions that inhibit corrosion. The residual hexavalent chromium in the film will repassivate any areas on the surface that become compromised due to chemical or mechanical damage to the area. This property is referred to as "self-healing."

The Institute selected three alternatives for study: molybdates, trivalent chromium compounds, and mineral tie-coat.

- **Molybdate-based coatings** inhibit corrosion by forming a protective oxide layer on metal.
- **Trivalent chromium passivates** exist in several types. They vary in appearance, performance characteristics, thickness of the coating, and other characteristics.

- **The mineral tie-coat** process is a patented method of applying a thin mineral film on the surface of metal parts. It involves cleaning and conditioning the surface to be plated, immersing it in a sodium silicate solution, and then electrodepositing a mineral coating. The reaction between the coating and the metal surface forms a new protective surface.

For each alternative, the Institute assessed health, environmental, technical, and cost criteria.

- **Health.** All the alternatives offer significant improvements over hexavalent chromium from the perspective of carcinogenicity and occupational exposure. Chemicals used in the trivalent chromium passivation process may pose skin irritation/sensitization hazards similar to those used in the hexavalent chromium process.
- **Environment.** All of the alternatives offer significant improvements in terms of their environmental impact, although chemicals used in some molybdate formulations are toxic to aquatic life.
- **Technical criteria.** Performance criteria of interest for passivation of zinc include corrosion resistance, heat resistance, torque/tension performance, and appearance.
    - Several technical evaluations have concluded that molybdates do protect against corrosion, but do not perform as well as hexavalent chromium passivation on this metric. Trivalent chromium may be inferior, equal, or superior to hexavalent chromium on this metric, depending on the thickness of the coating, the plating method, the additives, and whether a topcoat was used. According to the manufacturer, mineral tie-coat has superior corrosion resistance when used with a topcoat.
    - Trivalent chromium compounds do not have the "self-healing" properties of hexavalent chromium, and require a sealer/topcoat in order to offer the same level of corrosion resistance. The manufacturer of the mineral tie coat process claims that it is equal to or better than hexavalent chromium in corrosion resistance (with topcoat), heat resistance, and torque/tension performance.
    - Trivalent chromium coatings differ in appearance from hexavalent chromium films. For most applications, color is a matter of user preference rather than of performance. In cases where a specific color is required, topcoats or sealers can be used to achieve the desired effect.
    - The molybdates offer better heat resistance than hexavalent chromium.
- **Cost.** Little cost information is available for these alternatives. One analysis indicated that a molybdate-based process would be similar to a hexavalent chromium process in terms of labor and capital, more expensive for chemicals and energy, and less expensive for waste processing.

DEHP

Di (2-ethylhexyl) phthalate (DEHP) is a synthetic organic chemical that is used primarily as a plasticizer to impart flexibility to rigid plastics such as PVC. It belongs to the class of chemicals known as phthalates, which are used primarily as plasticizers in PVC plastics in a range of applications. DEHP is used in a wide variety of flexible plastic products.

DEHP is classified by the U.S. EPA as a probable human carcinogen (Class B2). In 2000, IARC changed its classification for DEHP from Group 2A ("possibly carcinogenic to humans") to Group 3 ("cannot be classified as to its carcinogenicity to humans"). Animal studies have found that DEHP is toxic to the male reproductive system. When DEHP is metabolized in the human body, it produces compounds that are likely to be reproductive toxicants.

DEHP can be released to the environment during its production, distribution and incorporation into PVC. DEHP is also released when PVC material is heated or comes into contact with certain media. DEHP is not chemically bound into the polymer matrix and therefore can migrate out of the polymer. It is especially likely to migrate out of the polymer in the presence of fatty solutions. Indoor releases of DEHP to the air from plastic materials, coatings, and flooring in home and work environments can lead to higher indoor levels than are found in the outdoor air.

Use of DEHP in flexible PVC medical devices is a significant source of exposure, especially in neonatal care. The National Toxicology Program (NTP) has expressed serious concern about reproductive toxicity in male infants who are exposed to DEHP in medical care. The Food and Drug Administration has recommended that health providers consider using alternatives to DEHP-containing medical devices when high-risk procedures are to be performed on male neonates, pregnant women who are carrying male fetuses, and peripubertal males.

The Institute assessed alternatives to DEHP in PVC in three categories: medical devices for neonatal care; resilient flooring; and wall coverings. Because DEHP is used primarily as a plasticizer in PVC plastics, two types of substitutions may be relevant: substitution of an alternative plasticizer for use with PVC, or use of a different material that does not require addition of a plasticizer. For each application, the Institute examined alternatives in both categories.

Resilient flooring

Resilient flooring is defined as tile and sheet materials that have the ability to return to their original form after compacting. The Institute assessed alternative plasticizers for use in PVC flooring, as well as alternative flooring materials.

Alternative plasticizers

The Institute assessed four alternative plasticizers for use in resilient flooring: di (2-ethylhexyl) terephthalate (DEHT), di isononyl phthalate (DINP), dipropylene glycol dibenzoate (DGD), and di (2-ethylhexyl) adipate (DEHA).

- **Health.** All the alternatives appear to be superior to DEHP from the perspective of reproductive toxicity, although some evidence exists that DEHA may be toxic to the developing fetus. None of the alternatives has been classified as to carcinogenicity in humans, but there is evidence that DINP is carcinogenic in rodents.
- **Environment.** All of the alternatives are less bioaccumulative than DEHP. DEHA is less persistent in sediment and less toxic to fish than DEHP; the other plasticizers are similar to DEHP for these parameters.
- **Technical criteria.** Technical parameters of interest for alternative plasticizers in resilient flooring include volatility, ease in compounding, tensile elongation, compatibility with PVC, and loss of plasticizer during manufacture and use. All the alternatives are comparable with DEHP from the perspective of volatility and tensile elongation. All except DEHT are comparable to DEHP with regard to compounding, and all except DEHA are comparable to

DEHP with regard to PVC compatibility. DINP has greater emissions during use, DEHA is inferior with regard to emissions during both manufacturing and use, and DGD has unknown properties on this metric.

- **Cost.** All the alternative plasticizers are comparable in cost to DEHP for resilient flooring applications on a functional equivalence basis.

Alternative materials

The Institute assessed three alternative flooring materials: natural linoleum, cork, and polyolefin.

- **Health.** Many studies have examined the human health and environmental implications of choice of flooring materials. Most of these studies examine the entire life-cycle of the product, from production to disposal. In general, these analyses favor the alternatives over DEHP/PVC flooring. Polyolefin flooring has the advantage of very low VOC emissions during use.
- **Environment.** Linoleum and cork are derived from sustainable materials and are biodegradable, making them superior to DEHP/PVC on these metrics. Cork offers the additional advantage that it can be installed without the use of adhesives. Linoleum has less impact on energy use from a life cycle perspective than DEHP/PVC flooring.
- **Technical criteria.** Technical criteria of interest for flooring applications include the availability of a range of colors and patterns; ease of maintenance; and recyclability. Linoleum and polyolefin flooring materials offer a range of colors and patterns that make them similar to DEHP/PVC in this regard, while cork is more limited in this respect. Ease of maintenance is generally similar across all the options. Polyolefin flooring is recyclable; linoleum and cork are not.
- **Cost.** The alternatives are generally similar to DEHP/PVC in purchase and installation cost, although costs vary depending on application. All the alternative materials have a longer expected life span than DEHP/PVC, further decreasing the overall cost.

Medical devices for neonatal care: sheet and tubing applications

Two distinct categories of medical devices used for infants in neonatal intensive care facilities were the focus of this study: bag/sheet devices, and tubing. The Institute investigated both alternative plasticizers and alternative materials for this application.

Alternative plasticizers

The Institute assessed five alternative plasticizers for use in medical devices.

- **Trioctyl trimellitate (TOTM)** is a clear, oily liquid that is a high production volume plasticizer in the US. In the medical device industry, TOTM is currently used primarily in blood and bag infusion sets.
- **Di (2-ethylhexyl) adipate (DEHA)** has properties that make it a useful plasticizer for materials used to store medical solutions that must be kept cold.
- **Butyryl trihexyl citrate (BTHC)** is a plasticizer specifically designed for use in medical articles, especially blood storage bags.

- **Di (isononyl) cyclohexane-1,2-dicarboxylate (DINCH)** is the hydrogenated product of the corresponding di C9 phthalate ester (DINP).
- **Di isononyl phthalate (DINP)** is currently used as a plasticizer in medical tubing devices.

TOTM, DEHA, BTHC, and DINCH are applicable for use in bag/sheet devices. Based on their elastic recovery properties, DEHA is also applicable for use in tubing, and DINP was assessed for use in tubing only. For each of these alternatives, the Institute assessed health, environmental, technical, and cost criteria.

- **Health.** All the alternatives are superior from the perspective of carcinogenicity and reproductive toxicity, although there are grounds for concern about DINP and DEHA, as noted above. The alternatives are generally superior with regard to skin, eye, and respiratory irritation, with some exceptions.

  A key issue associated with potential health effects is the ability of a plasticizer to exude from the polymer matrix as well as its potential to produce metabolites of concern. DEHP is lipid soluble and therefore is likely to exude out of the polymer when exposed to a lipid-soluble solution. TOTM, BTHC and DINCH appear to be less likely to migrate out of the polymer in the presence of lipid-soluble medical solutions. DINP appears to be similar to DEHP in this regard, and the potential for DEHA to migrate is not well defined.

  Little information is available on the health effects of metabolites associated with the alternatives assessed. The exception is BTHC, which can be metabolized to butyric acid, a chemical that is associated with negative impacts on the GI tract, liver and skin.

- **Environment.** All the alternatives are equally or less persistent in sediment compared to DEHP (DINCH persistence is unknown). The alternative plasticizers studied are all superior from the bioaccumulative and aquatic toxicity perspectives, with the exception of DINP, which has aquatic toxicity similar to that of DEHP. The aquatic toxicity of BTHC is not known.
- **Technical criteria.** Important criteria for both sheet/bag and tubing applications include flexibility when cold, clarity, compatibility with PVC, sterilizability, and plasticizer loss during manufacture and use. In addition, elastic recovery is an important parameter for tubing applications. Some important differences between DEHP and alternatives are noted below:
  - TOTM is inferior on measures of cold flexibility; DEHA is similar; and the other three alternatives are superior to DEHP on this measure.
  - DEHA is less compatible with PVC than DEHP.
  - BTHC is not steam sterilizable, while DINP tolerates steam sterilization better than DEHP. The sterilizability of DINCH is not known.
  - TOTM, BTHC, and DINCH are superior to DEHP on measures of plasticizer loss during use. DEHA and BTHC are inferior to DEHP on measure of plasticizer use during manufacture.
- **Cost.** Costs of DEHA and DINP are similar to those of DEHP, while the other alternatives are more expensive.

Alternative materials

The Institute evaluated five alternative materials for medical devices: ethyl vinyl acetate (EVA), polyolefins (polyethylene and polypropylene), glass, silicone, and polyurethane. Some of these could replace DEHP/PVC sheets, while others could replace DEHP/PVC tubing.

- **Ethyl vinyl acetate (EVA)** is a copolymer blend of vinyl acetate, ethylene, and ethyl acetate that has been used for many years in medical sheet applications. EVA bags are also used for custom mixing of drugs by pharmacies.
- The **polyolefins** polyethyelene (PE) and polypropylene (PP) are widely used compounds that are valued for their flexibility, transparency and toughness.
- **Glass** was commonly used to store medical solutions prior to the extensive use of plastics.
- **Silicone** is a synthetic rubber that can be used in medical tubing. Silicone tubing is translucent, biologically inert, and inherently flexible.
- **Thermoplastic polyurethane (TPU)** is used in tubing applications.

The Institute assessed health, environmental, technical and cost criteria for each alternative.

- **Health.** All the alternative materials are superior to DEHP/PVC from the perspective of leaching plasticizers with known health concerns, since none of the alternatives utilize plasticizers. While rigid and more difficult to handle due to the potential for breakage, glass is the most inert material available on the market today for health care.
- **Environment.** All the alternative materials are superior to DEHP/PVC materials plasticized with DEHP in the sense that they do not generate hazardous chlorinated organic compounds when incinerated. However, there is significant variation among the alternatives in level of toxicity over the life cycle of the product. Manufacture of TPU involves use of diisocyanates that are listed on the Massachusetts Science Advisory Board's list of more hazardous chemicals. Incineration of TPU also releases hazardous chemicals including isocyanates and hydrogen cyanide. On measures of recyclability, glass is far superior to PVC containing DEHP; other alternatives are equally or more difficult to recycle compared with DEHP/PVC.
- **Technical criteria.** Using materials that are inherently flexible eliminates one of the key problems with DEHP/PVC, the potential for the material to become brittle due to loss of plasticizer. Therefore, the alternatives may have longer shelf lives than their DEHP/PVC counterparts and the possibility of leached plasticizer entering the body is eliminated. Other performance criteria of interest for these uses include elastic recovery, cold flexibility, sterilizability, gas permeability, and manufacturability. Some key differences between the alternative materials and DEHP/PVC are noted below.
    - TPU exhibits inferior elastic recovery.
    - Only silicone is superior to DEHP/PVC from the perspective of cold flexibility. Glass is not flexible.
    - Neither EVA nor polyolefin is appropriate for steam sterilization.
    - Manufacturability (i.e., the ease with which the material can be transformed into the finished product) is superior for glass, and inferior for EVA, silicone and TPU.

- **Cost.** Currently raw material prices and relative use costs for the alternatives vary relative to DEHP/PVC. However, costs of the alternatives are changing in response to increasing demand for and supply of DEHP- and PVC-free medical devices. Technical differences among materials can also be a source of cost savings. For example, EVA film can be manufactured at a thinner gauge than similar PVC film, thus reducing the per-item cost. For tubing applications, silicone and TPU can be used for longer periods of time than PVC/DEHP, thereby reducing the cost differential. Large hospital chains are also driving market changes, and cost reductions, by specifying PVC- or DEHP-free materials in their purchasing contracts.

Wall coverings

DEHP/PVC (vinyl) wall coverings are used in both commercial and residential settings for decorative and protective purposes. Vinyl wall coverings are popular because they are available in a wide array of patterns and colors and are both durable and scrubbable.

It is worth noting that there are viable process alternatives to vinyl wall coverings, including painted wall surfaces or using different wall materials (such as wood paneling). They differ significantly from wall coverings in terms of aesthetics, but can be functionally equivalent. These process alternatives were not included in the assessment.

Alternative plasticizers

The Institute assessed two plasticizer alternatives for use in wall coverings: DEHA and DINP.

- **Health.** As previously discussed, DEHA is potentially toxic to the developing fetus and DINP has been found to cause cancer in laboratory animals. The potential for exposure to DEHA is greater than for DEHP.
- **Environment.** DEHA is less persistent in sediment than DEHP, and DINP is similar to DEHP on this parameter. Both are less bioaccumulative than DEHP. DEHA is less toxic to fish than either DEHP or DINP.
- **Technical criteria.** Criteria of interest for wall coverings include volatility, compounding, tensile elongation (life of product), compatibility with PVC, and emissions (during manufacture and use). DINP is similar to DEHP on all measures. DEHA is inferior on measures of volatility, PVC compatibility, and emissions during manufacture and use. Compared with DEHP, DINP has better high temperature performance and extraction resistance, which improves is processability.
- **Cost.** Both plasticizers are similar to DEHP in cost per pound applied. Compared with DEHP, DINP processing emits lower levels of plasticizer mist from process equipment. As a result, less plasticizer is lost to the air and more retained in the product, yielding overall cost savings.

Alternative materials

The Institute assessed five categories of alternative materials: glass woven textiles, cellulose/polyester blends, wood fiber/polyester blends, biofibers, and polyolefins.

The Institute evaluated health, environmental, technical, and cost criteria for each of these alternative materials.

- **Health.** The primary concern with DEHP in wall coverings is exposure during manufacture and use. No plasticizer is emitted during manufacture or use of the alternative materials, but there may be other volatile organic emissions. In particular, the glass textile and polyolefin alternatives have similar potential VOC exposures compared to DEHP/PVC. Little information on exposure associated with the other materials was available.
- **Environment.** All the alternative materials except the polyolefins are derived from more sustainable materials than DEHP/PVC. Some offer the advantage of being recyclable and one alternative material (wood pulp/recycled paper) is compostable. Two of the alternative materials (BioFibers and polyolefins) are routinely coated with Teflon® finish, which may pose occupational and other hazards.
- **Technical criteria.** All the alternatives are similar to DEHP/PVC in ease of maintenance. Wood fiber/polyester and cellulose/polyester alternatives offer a range of colors and patterns similar to those available with DEHP/PVC.
- **Cost.** Most of the alternatives are comparable in price to high-end DEHP/PVC wall covering products, but are much more expensive than low-end vinyl.

Economic Assessment

Financial considerations are discussed within each alternatives assessment. The information presented for each case varies according to context. For example, the price of materials is an important parameter for some cases, while operation, maintenance, or disposal costs may be salient for others.

Specific lessons that can be drawn from the alternatives assessments conducted here include the following.

- Some alternatives can be adopted without any adverse effect on Massachusetts employment or competitiveness. The formaldehyde alternatives assessment, for example, shows that elimination of formaldehyde dry sterilant from use in Massachusetts hair salons would produce savings and make sanitation standards at Massachusetts hair salons consistent with those in the rest of the country. Similarly, Massachusetts schools could adopt alternatives to formaldehyde-fixed dissection specimens without increasing costs.
- Massachusetts manufacturers could gain market share through adoption of some alternatives. For example, some Massachusetts firms are working to produce DEHP-free medical devices. With growing demand for such devices, firms may have opportunities for growth in this area.
- Some alternatives require capital investment at the outset. For some technologies, this investment will pay for itself over time in reduced operating costs.
- In some cases, alternatives are more costly at this time (*e.g.*, PCE vapor degreasing solvent alternatives) and for many no firm cost conclusions can be reached without more information.

In addition, the Institute convened a group of economic experts to assess potential state-wide implications of adopting alternatives for employment in the Commonwealth and competitiveness of Massachusetts firms. The panel of experts worked with TURI to develop a framework for analysis of the economic implications within Massachusetts of alternatives adoption. This framework will assist users in analyzing likely economic impacts by clarifying the situational characteristics and factors that determine the outcome. Characteristics that may help to determine the economic implications of alternatives adoption include the size of the Massachusetts market in comparison with other markets, price sensitivity of consumers, nature of barriers to adoption, capacity of the workforce, and availability of useful and timely information.

Broader conclusions that emerged from the Institute's literature review and consultation with experts include the following.

- First, there is strong evidence that adoption of safer alternatives can produce economic benefits. This is a lesson from the experience of the TURA program, the literature on this topic, and some of the sectors considered in this report.
- There are some cases in which substituting chemicals or processes may have negative effects on some firms, even if there is a positive effect on the state economy more generally.
- There are many opportunities for government to support a positive economic outcome and to mitigate any negative effects for individual firms. In some instances, targeted assistance to industry can facilitate adoption of safer alternatives that will yield employment and competitiveness benefits over time.

Conclusions

The detailed information provided in this report should serve as a valuable resource for anyone interested in understanding the alternatives to the five chemicals that were examined in this study. The report is designed to be useful to policy makers, industry, public health and environmental professionals and advocates, and other stakeholders. In every case, at least one alternative was identified that was commercially available, was likely to meet the technical requirements of many users, and was likely to have reduced environmental and occupational health and safety impacts compared with the base chemical.

The active involvement of all stakeholders was key to the success of this project. Their expertise, willingness to collaborate and share perspectives, and review of the report were invaluable. The involvement of a wide range of stakeholders throughout the project resulted in a more accurate assessment, more valuable results, and increased understanding of the issues, challenges and perspectives among stakeholders. Stakeholder contributions to this project also revealed in detail the substantial investment firms have made in developing safer products. For example, efforts to reduce the negative impacts of formaldehyde in wood products have succeeded in producing formulations with greatly reduced off-gassing. Similarly, years of effort have been devoted to developing reliable lead-free electronics.

Many promising alternatives were identified during this study. Some of these will require further work to determine their practicality and applicability for specific applications. Such work will speed up the adoption of these alternatives, and could include detailed discussions with vendors and users, independent laboratory testing of technologies, pilot-scale industrial installations, supply chain workgroups and demonstration sites. The Institute has had success using these approaches for industrial toxics use reduction, and believes that there are many parallels for small businesses and consumer products.

The Institute's experience with this study has also yielded important lessons about the methodology of alternatives assessment. The experience of the Institute and the information contained in this report indicate that alternatives assessment is a useful approach to organizing information about chemicals and alternatives. The Institute encourages readers to build on the work that has been done in this study, both by conducting alternatives analyses on other chemical uses, and by working to refine and streamline this methodology.

Finally, this study will have been a success if it spurs discussion and debate. It is the Institute's hope that the information in this report will serve as valuable source material for those discussions.

Chapter 1. Introduction

Five Chemicals Alternatives Assessment Study

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1.1 Legislative Mandate and Context

The Toxics Use Reduction Institute was created by the Massachusetts Toxics Use Reduction Act of 1989 to assist industry, communities, and academia in their efforts to reduce the use of toxic chemicals while enhancing the economic competitiveness of businesses in the Commonwealth. Located at University of Massachusetts Lowell, the Institute provides research, training, technical support, laboratory services and grant programs in support of this mission.

In July 2005, the Commonwealth of Massachusetts requested that the Toxics Use Reduction Institute (the Institute) conduct a study to assess the feasibility of adopting safer alternatives for the following five chemicals:

- Lead
- Formaldehyde
- Perchloroethylene
- Hexavalent chromium
- di(2-ethylhexyl)phthalate (DEHP).

The text of the legislative mandate to the Institute is as follows:

> "For an assessment at the Toxics Use Reduction Institute on the feasibility of adopting chemical or technological alternatives for the following toxic or hazardous substances: lead, formaldehyde, perchloroethylene, hexavalent chromium, and di(2-ethylhexyl) phthalate (DEHP); provided, that the assessment shall, for each named toxic or hazardous substance, identify:
>
> (1) significant uses of the toxic substance in manufacturing, consumer products and any other applications;
>
> (2) potential human health and environmental impacts;
>
> (3) any alternative chemicals or technologies, both proven and emergent, and an analysis of their potential to serve as substitutes for any of the toxic or hazardous substances listed above, which shall include an assessment of:
>
> a. specific applications of any alternative chemical or technology;
>
> b. potential impacts on the environment, human health, workers, employment level and economic competitiveness of the commonwealth

from adopting and implementing any alternative chemical or technology as substitutes;

c. the economic opportunities or feasibility of adopting and implementing any alternative chemical or technology as a substitute including, but not limited to, consideration of the potential effects on capital, operating and production unit costs, and product price, to result from the substitution;

> and provided further, that the Institute shall report its findings to the joint committee on environment, natural resources and agriculture by July 1, 2006."

The Institute's sixteen years of experience in identifying and evaluating safer substitutes for toxic chemicals in industry and commerce has proved to be a valuable foundation for undertaking this project. Examples of major activities that contribute directly to our capabilities to perform these alternatives assessments are:

- Development of the Toxics Use Reduction Planner curriculum, and the training of over 1000 professionals in toxics use reduction methods;
- Establishment of the Surface Solutions Laboratory, which has done research on safer substitutes for hundreds of cleaning processes that were using toxic solvents such as perchloroethylene;
- Basic research, both in-house and with outside scientists, into new chemical alternatives;
- Establishment of the New England Lead Free Electronics Consortium to develop lead-free electronics in response to European Union (EU) directives;
- Establishment of the Wire and Cable Supply Chain Initiative, to help this Massachusetts industry group meet EU directives and adopt safer materials; and
- Ongoing policy research into alternatives assessment methodologies, in order to improve and refine the techniques used to perform an alternatives assessment.

In response to this Legislative request, the Institute refined its "alternatives assessment" methodology to evaluate the feasibility of alternatives to the five chemicals based on technical, financial, and environmental, health and safety considerations. In addition, the Institute investigated possible economic impacts on the Commonwealth of adopting alternatives.

This report presents the results of the study. It provides an overview of how the five chemicals are used, and detailed information on selected alternatives for several high priority uses of each of the five chemicals. The focus of this report is on providing factual information on each alternative that can help readers to understand the availability and potential viability of alternatives for each use. The study does not rank the alternatives in relation to one another. Rather, it compares each alternative with the studied chemical, and provides information that will allow users to make better decisions concerning these alternatives by applying their own unique application-specific criteria.

1.2 Goals and Objectives

The goals of the study support the intention of the legislative request to:

- Develop a methodology for assessing alternatives;
- Involve stakeholders in setting priorities;

- Perform a full alternatives assessment for particular uses and alternatives for the five chemicals evaluating:
    - Technical feasibility,
    - Economic feasibility, and
    - Potential environmental, health and safety impacts;
- Evaluate the economic influences that should be considered when adopting alternatives assessment strategies; and
- Produce an objective, transparent, and useful report for the Legislature, which will also be available to industry and the public.

Chapter 2. Approach and Methodology

Five Chemicals Alternatives Assessment Study

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2.1 Approach

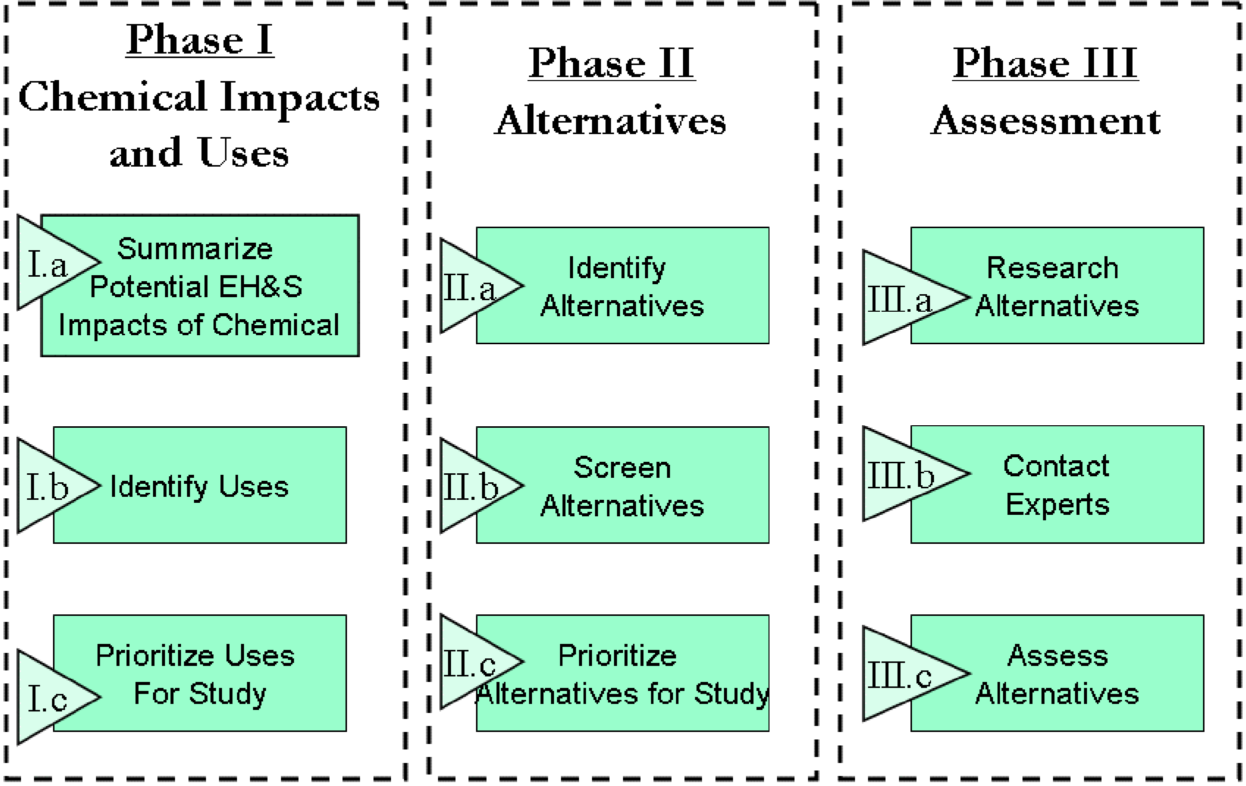
This chapter presents the approach taken by the Institute to perform the study and describes the methodology used to assess alternatives. The Institute's approach was designed to achieve the goals stated in Section 1.2, while recognizing the constraints of time and resources. As a "pilot project" the approach had to be flexible, allowing for changes in the methodology as it was implemented. As a result the project outcomes are both a more robust assessment methodology and a series of informative alternatives assessments for the five chemicals.

A consistent process for setting priorities and evaluating the alternatives for the five chemicals was first established. The methodology for this study is outlined in a companion document entitled "Five Chemicals Study Methodology - Alternatives Assessment Process Guidance" (see Appendix A). That document reflects the original methodology developed, and provides guidance to those conducting assessments. The guidance document was especially important because, due to the short timeline and broad scope of the project, different Institute staff members and their technical experts conducted the alternatives assessments simultaneously.

It is important to note that this study was not conducted in a manner designed to assess the relative safety of one alternative over the other. Rather, alternatives were compared to the study chemical as a baseline.

The following graphic illustrates the phased approach that was used in this study.

Figure 2.1: Project Approach



Phase I focused on characterizing the potential environmental health and safety impacts of each chemical and identifying the priority uses in Massachusetts. In Phase II the Institute identified alternative chemicals and/or technologies for those priority uses and utilized a set of environmental, health and safety screening criteria to determine those alternatives that warranted assessment. In addition, where there were more potentially feasible alternatives than could be assessed in this study, additional criteria were used to determine those alternatives that were a high priority for assessment. Each of these two initial phases was performed under an aggressive schedule so as to allow as much time as possible for completion of the assessments.

Phase III represented the bulk of the assessment work, involving evaluation of the technical financial, and environmental and human health and safety parameters of the identified alternatives.

2.2 Stakeholder Involvement

To produce useful results in the time available it was necessary to narrow the scope of the project to areas that would have the greatest positive impact on Massachusetts. The Institute evaluated existing information and sought input from Massachusetts stakeholders on which chemical uses and alternatives assessments would provide the most valuable and useful information for them. Representatives of Massachusetts companies, government, non-government environmental, health and labor organizations, and industry associations participated in a series of stakeholder meetings to assist the Institute in identifying significant uses, both in manufacturing and in products, and in prioritizing the uses and alternatives to be assessed.

Organizations participating at stakeholder meetings represented a wide range of Massachusetts interests, including but not limited to:

- Alliance for a Healthy Tomorrow
- Associated Industries of Massachusetts
- Astro Chemical
- Boston Scientific Corporation, Inc.
- Children's Hospital of Boston
- Clean Water Action
- Greater Boston Physicians for Social Responsibility
- Haemonetics Inc.
- Korean Dry Cleaners Association
- M/A-COM, a subsidiary of Tyco Electronics
- Massachusetts Public Interest Research Group
- Massachusetts Chemistry and Technology Alliance
- Massachusetts Coalition for Occupational Safety and Health
- Massachusetts Department of Environmental Protection
- Massachusetts Office of Technical Assistance
- Massachusetts State Legislature
- New England Fabric Care Association
- New England Korean Dry Cleaners Association
- North Shore Labor Council
- Rohm and Haas Electronic Materials
- Saint-Gobain
- Solutia
- Teknor Apex
- We Care Cleaners
- Western Massachusetts Coalition of Occupational Safety and Health

Stakeholder participants provided valuable contributions in three areas. First, they helped to refine the methodology and project plan. Second, they helped to narrow the scope of the project to areas that would have the greatest positive impact on Massachusetts. Third, stakeholders provided their own experience, expertise, and contacts to supplement the Institute's science and technical research. Comments were solicited at meetings, through email and telephone conversations, and through a draft report review process.

Four structured process meetings were held, as well as several less formal topic-specific meetings that addressed a specific method, chemical, or economic topic. The structured process meetings were held in Lowell and each were attended by close to forty participants:

1. September 26, 2005 – Methodology and Project Plan
2. October 21, 2005 – Use Prioritization
3. November 9, 2005 – Alternatives Prioritization
4. April 11, 2006 – General Project Update

While, in general, the input from stakeholders varied depending on their perspective, concerns and interests, during the use prioritization phase there were some common themes that emerged, including:

- A high priority should be placed on uses that are associated with higher potential exposure to the public and/or workers in small businesses.
- A low priority should be placed on uses where alternatives are already being readily adopted, or where significant research on alternatives is being carried out by others.

Stakeholders assisted in the identification of experts in academia, industry, national trade associations, labor, and environmental and health groups. Institute staff conducted on-site visits with specific industries to identify pertinent manufacturing and product performance criteria, as well as to obtain industry-specific financial information. For example, project staff visited several drycleaners using perchloroethylene and alternatives, and a resilient flooring manufacturer using DEHP and alternative plasticizers and materials. Certain industry experts met with Institute staff to address such topics as formaldehyde chemistry in adhesives, technical criteria for shooting range ammunition, and the toxicology of certain plasticizers.

The stakeholder meetings and follow-up communications were very helpful in identifying high-priority uses and alternatives for assessment, as well as in ensuring the technical accuracy of Institute findings. Broad and detailed information collected at each stage was shared and posted on the project website at www.turi.org. At meetings focused on prioritization, each chemical was discussed separately, reviewing its hazards, uses and potential alternatives. Specific input from stakeholders on each chemical and use is included in the chemical chapters of this document.

2.3 Phase I: Chemical Impacts and Uses

2.3.1 Potential Impacts of Chemicals (Phase Ia)

Potential human health and environmental impacts associated with the use of the five chemicals were summarized as part of the prioritization process. This information was obtained primarily from public databases and published reference sources. In addition, peer-reviewed scientific journals, other published reference materials, industry trade group resources (publications and web sites) and advocacy group resources (publications and web sites) were used to provide more depth or to identify newer, emerging information. The Institute did not conduct a comprehensive review of toxicological studies.

The objective of this summary was to provide background information on the chemical, highlight environmental, health and safety issues, and provide a baseline against which the alternatives could be compared.

2.3.2 Identify Uses (Phase Ib)

Uses of chemicals in Massachusetts range from manufacturing processes to services to consumer products. For each of the five chemicals considered in this study, the majority of the major uses of the chemical were identified. This information is included in Appendix B. The range of uses identified for each chemical was so wide and varied that the Institute was not be able to evaluate all of them in the short time span allowed for this project. It was therefore necessary to narrow the scope to evaluate uses that were considered a high priority for Massachusetts (Phase I.c).

In order to prioritize uses for further study, information was gathered from the literature and experts to determine the following:

- Major suppliers of the chemical
- Major derivatives, components and/or end products that incorporate the chemical or use the chemical as a feedstock, and their manufacturers - this considered the Massachusetts, domestic, and international markets
- Major distributors, retailers, or customers of end product, focused on Massachusetts customers
- Functionality requirements of chemical or component or end-product - for example, why is the chemical used and what is it used for?
- Relevant stakeholders, including businesses, industry associations, environmental, public health, and labor organizations.

2.3.3 Prioritize Uses (Phase I.c)

Meetings with Massachusetts stakeholders, as described in Section 2.2, were organized to provide information to stakeholders on the chemical use prioritization criteria, review the list of uses researched by the Institute, and solicit input from stakeholders on priority uses for further investigation.

The Institute's final selections of high priority uses for study are listed in Table 2.3 A. The final selections were made based on the following criteria:

1. Importance to the Commonwealth of Massachusetts:
    - Use in manufacturing: Total quantity of chemical used in manufacturing operations in Massachusetts
    - Use in consumer products: Total quantity of chemical used in products sold in Massachusetts.
2. Potential availability of alternatives.
3. Exposure potential (environmental, occupational, and public health).
4. Potential value to Massachusetts businesses and citizens of the alternatives assessment results. Specifically, the preferences of the pertinent stakeholders for each chemical were given priority.

In addition, for each chemical the Institute attempted to select at least one use that was applicable to each of three end users, *i.e.*, Massachusetts manufacturers, small businesses and consumers, when making the final selection of priority uses to study. A detailed discussion of the prioritization process for each chemical is included in the relevant chemical chapter.

Table 2.3.3 : High Priority Uses

Chemical	Final High Priority Uses for Study
Lead	• Ammunition for shooting ranges • Wheel weights • Fishing sinkers • Heat stabilizers for PVC wire and cable coatings

Chemical	Final High Priority Uses for Study
Formaldehyde	• Sanitary storage in barbering and cosmetology • Preserved educational specimens for dissection • Building panels
Perchloroethylene	• Dry cleaning • Vapor degreasing • Automotive aerosols (brake, external and internal engine, and tire cleaners)
Hexavalent Chromium	• Decorative chrome electroplating • Hard chrome electroplating • Passivation of zinc
DEHP	• Resilient flooring • Medical devices for neonatal care (sheet and tubing applications) • Wall coverings

2.4 Phase II: Alternatives

2.4.1 Identify Alternatives (Phase II.a)

Alternatives to toxic chemicals may include drop-in chemical substitutes, material substitutes, changes to manufacturing operations, changes to component/product design, and other technological solutions. Existing and emerging alternatives were identified for each of the high priority uses of the chemicals. In addition, industry specific performance requirements were identified.

Sources of information on available and emergent alternatives included trade associations, manufacturers, U.S. Environmental Protection Agency (EPA) documents and programs, municipal, state and federal pollution prevention research centers, literature and internet searches, and other technical experts. In addition to experts at the Institute, experts from the University of Massachusetts Lowell, other universities, industry, medicine and many other organizations were consulted. As a result, more than 200 potential alternatives were identified for the 16 different use categories of the 5 chemicals. Each alternative typically consisted of several different chemical constituents.

2.4.2 Screen Alternatives

To eliminate from further study any chemical alternatives that would pose a high risk to the environment or human health, alternatives were subjected to an initial environmental, health and safety (EH&S) screen. If a specific alternative was determined to be persistent, bioaccumulative and toxic ("PBT"), a known or probable human carcinogen, or on the TURA Science Advisory Board's (SAB) 1999 More Hazardous Chemicals list, it was eliminated from further consideration. In order to be screened out as a "PBT" a substance needed to exceed the EPA criteria for two of the three PBT indicators (very persistent, very bioaccumulative, and high concern for toxicity). The PBT screening process utilized the EPA's PBT Profiler, a predictive modeling tool. Chemicals that are listed in either the EPA Group A or B, or the International Agency on Research of Cancer (IARC) Group 1 or 2A (carcinogenic or probably carcinogenic to humans) were also eliminated from further study. In the SAB list, "hazard" includes inherent toxicity, potential for exposure through dispersal in the work place (based on the physico-chemical properties of the chemicals such as vapor pressure) and indicators of safety of use (*e.g.,* flammability).

The initial EH&S screen was only applied to the substances present in the alternative formulation or product, not to feedstock materials upstream, or breakdown products downstream. For example, if an alternative material is a polymer made from a carcinogenic monomer, it would not be screened out during this initial phase. A detailed discussion of the screening criteria is included in Appendix A.

2.4.3 Prioritize Alternatives for Study

At this stage, all available alternatives that had passed the EH&S screening were evaluated to determine which alternatives would be assessed fully. The objective of this step was to select for full assessment a small number of alternatives (typically 6 or fewer) that appeared most likely to be feasible and safer. The following criteria were considered in prioritizing the alternatives to be assessed:

1. Performance: Known performance of the alternative, which could include maintenance and durability as well as specific performance requirements and potential for future performance enhancements.
2. Availability: Number of suppliers or manufacturers and volume produced.
3. Manufacturing Location: Products or materials manufactured in Massachusetts were considered a higher priority.
4. Environmental and human health and safety issues: Concerns identified during the initial EH&S screening.
5. Global Market Effect: Pending or existing global restrictions
6. Classes of Similar Alternatives: Where several similar alternatives were identified, one representative of that type was chosen for further study.
7. Cost: Compared to the existing chemical and considering the potential for future cost reductions associated with increased production volume. Includes consideration of raw material costs, storage and handling costs, disposal costs, etc.
8. Value to Massachusetts Stakeholders: If an alternative was of particular interest to one or more stakeholder, or there appeared to be a high value to Massachusetts for the alternative to be included in the assessment, it was given a higher priority.

Meetings with stakeholders, as described in Section 2.2, were organized to provide information on the alternatives prioritization criteria, review the list of alternatives researched by the Institute, and solicit input from stakeholders on alternatives for the assessment phase of this study. The final list of alternatives for full assessment is listed in Table 2.4.3.

Table 2.4.3 : High Priority Alternatives

Chemical	High Priority Use	High Priority Alternatives to be Assessed
Lead	Ammunition for Shooting Ranges	1. Bismuth 2. Copper 3. Iron 4. Tungsten 5. Zinc
	Wheel Weights	1. Copper 2. Steel 3. Tin 4. Zinc and zinc/copper/aluminum alloy (ZAMA)
	Fishing Sinkers	1. Bismuth 2. Steel 3. Tin 4. Tungsten 5. Ceramic
	Heat Stabilizers for PVC Wire and Cable Coatings	1. Calcium zinc 2. Barium zinc 3. Magnesium zinc 4. Magnesium aluminum hydroxide carbonate hydrate 5. Magnesium zinc aluminum hydroxide carbonate
Formaldehyde	Sanitary Storage in Barbering and Cosmetology	1. Process change to eliminate use of paraformaldehyde “Steri-dri” sterilants 2. UV sterilization chamber
	Preserved Educational Specimens for Dissection	1. Specimens in Formalternate (propylene glycol-based) 2. Specimens in Wardsafe (gluteraldehyde-based) Specimens in STF Preservative (diazolidinyl urea-based) 3. Virtual/Video dissection
	Building Panels	1. Wood plywood panels (Purebond) made by Columbia Forest Products (soy adhesive binder) 2. Recycled paper-based panels made by Homasote (paraffin wax binder) 3. Wood fiber-Portland Cement panels made by Viroc 4. Plastic-wood composite panels by JER Envirotech
Perchloro-ethylene	Dry cleaning	1. Hydrocarbon (Exxon Mobil DF-2000) 2. Substituted aliphatic glycol ethers (Rynex) 3. Volatile Methyl Siloxane (GreenEarth) 4. Wet cleaning – traditional (PowerBrite detergent) 5. Wet cleaning - Icy Water (DWX 44 detergent) 6. Wet cleaning - Green Jet (DWX 44 detergent) 7. Liquid CO_2
	Vapor Degreasing	1. N-propyl bromide (Ensolv) 2. Volatile methyl siloxane (Dow OS 10) 3. HFC (Micro Care Flux Remover C) 4. HFC (Dupont Vertrel MCA) 5. Aqueous cleaning

Table 2.4.3 : High Priority Alternatives

Chemical	High Priority Use	High Priority Alternatives to be Assessed
	Automotive Aerosols (brake, external and internal engine, and tire cleaners)	18 different commercial products, based on: 1. Aqueous (water and detergent) 2. Silicone 3. Glycol ethers 4. Hydrocarbons, petroleum distillates 5. Toluene 6. Xylene 7. Heptane 8. Citrus based terpene (d-limonene)
Hexavalent Chromium	Decorative Chromium Electroplating	1. Trivalent chromium plating baths 2. Low temperature arc vapor deposition of trivalent chromium
	Hard Chromium Electroplating	1. Thermal sprays: high velocity oxy-fuel and plasma sprays 2. Weld facing methods and micro-arc welding 3. Heat treatments and plasma nitriding 4. Vapor deposition 5. Nanocrystalline coatings 6. Trivalent chromium plating baths
	Zinc galvanized steel passivation	1. Molybdates 2. Trivalent chromium compounds 3. Mineral tie-coat
DEHP	Resilient Flooring	1. DEHT, di 2-ethylhexyl terephthalate 2. DINP, di (isononyl) phthalate 3. DGD, dipropylene glycol dibenzoate 4. DEHA, di 2-ethylhexyl adipate 5. Natural linoleum 6. Cork 7. Polyolefin
	Medical Devices for Neonatal Care: Sheet Applications	1. TOTM, tri-2-ethylhexyl trimellitate 2. DEHA, di (ethylhexyl) adipate 3. BTHC, butyryl trihexyl citrate 4. DINCH, di (isononyl) cyclohexane-1,2-dicarboxylate 5. EVA 6. Polyolefins 7. Glass
	Medical Devices for Neonatal Care: Tubing Applications	1. DINP, di (isononyl) phthalate 2. DEHA, di (ethylhexyl) adipate 3. Silicone 4. Thermoplastic polyurethane (TPU)
	Wall Coverings	1. DEHA, di (ethylhexyl) adipate 2. DINP, di (isononyl) phthalate 3. Glass woven textiles 4. Wood fiber/Polyester 5. Cellulose/polyester blends 6. Biofibers 7. Polyolefins

Some alternatives, particularly those comprised of single chemicals, were assessed as generic alternatives (*e.g.,* TOTM plasticizer or steel fishing sinkers). Other alternatives vary considerably depending on the precise formulation or manufacturer. In these cases a representative product was assessed (*e.g.,* products for aerosol brake cleaning and educational specimens for dissection). The choice of a particular manufacturer's product as representative does not constitute an endorsement of that product, or indicate that other similar products are not worthy of further consideration by users.

2.5 Phase III: Alternatives Assessment

Information for each aspect of the assessment – technical, environmental, human health and safety, and financial – was collected and reviewed. The specific types of information and procedures for evaluating them are described in the following sections. When all available data had been collected for each alternative, the information was reviewed and summarized in a qualitative summary table for that particular use.

For each critical parameter in the summary table, a qualitative assessment of "better than" (**+**), "similar/equivalent" (**=**), or "worse than" (**-**) the chemical being studied was indicated. Where insufficient information was available to make a determination, a "**?**" was indicated.

It should be noted that these are approximate indicators only, and that all parameters should not be considered equal (for example, most users would not consider "carcinogen" with equal weight as "irritant.") For these reasons, it is not appropriate to simply add up the total number of **+**, **-** , and **=** in order to determine the "best" alternative. Users should look to the summary tables, and the supporting assessment text and tables, for guidance in conducting their own assessment of feasibility and preferred alternatives. Their own assessments will include personal or corporate values, priorities, levels of concern/acceptability and situation-specific modifications and additions to the assessments included in this report.

2.5.1 Technical Feasibility

The study identified application-specific performance requirements that were required for each use – including longevity, key performance requirements, key physical characteristics and key quality parameters. One primary source of this information was industry/user experience with the chemicals and their substitutes. User comments and review were sought from manufacturers, trade associations and customers who use the chemical or its derivatives.

The quality of performance information that the Institute was able to obtain on the alternatives varied considerably among uses. For some uses information was obtained from published robust studies or directly from several users of the alternatives or technical experts. For other uses assessments relied on information provided by product manufacturers. This directly impacts the degree and nature of follow-up that would be required for a user to make a determination of technical feasibility for their unique application.

Where appropriate, the study also included readily available information on life cycle considerations, such as maintenance requirements, although it is important to note that this study did not include a comprehensive life cycle assessment.

The summary tables include a relative assessment of key performance parameters as appropriate for each use, compared with the reference chemical or product, using the symbols discussed above.

2.5.2 Financial Feasibility

Financial information was sought for each alternative (see Appendix A for table of financial assessment parameters). Data sources included manufacturers, stakeholders, the Chemical Economics Handbook and other publicly available reference sources. The amount of financial information available for each use and alternative varied widely. In many cases, particularly for emerging alternatives with few or no current instances of actual use, no hard cost information was available; if so, this is indicated in the discussion of those particular alternatives. In other cases, sufficient cost information exists to conclude that the alternative is either more or less costly than the current chemical use; again, this is noted in the discussion where appropriate.

Other significant barriers to determining financial feasibility of alternatives include: manufacturers' reluctance to share cost information, facility or application-specific nature of many costs, and the fact that cost comparisons *today* may not be the final answer *tomorrow* for technologies not yet widely adopted, since economy of scale and market size will often reduce costs. This issue is discussed more thoroughly in Chapter 8.

For these reasons, the financial assessments should be viewed as a preliminary look at potential impacts as a result of adopting an alternative. Those wishing to conduct a more thorough financial analysis will need to include application- and facility-specific impacts, including the cost of raw material, capital improvements and new equipment, processing changes, waste disposal, energy, worker health and safety protection, permitting, and other life cycle costs, such as end-of-life product management. Tools and information for "total cost assessment" and other financial assessment approaches may be found in many existing publications (contact the Institute for more information).

2.5.3 Environmental and Human Health Assessment

The Institute assessed each alternative for its impact on human and environmental health relative to the chemical of concern. A set of pertinent environment, health and safety (EH&S) parameters was evaluated. The list of the parameters and their associated metrics, concern levels and primary data sources is presented in Appendix A. The Institute did not perform a detailed toxicological review for each alternative. Rather, the study relied on information obtained from authoritative bodies[1], with the most recent validated data presented first or data that has been referenced by a US governmental agency such as the Environmental Protection Agency (EPA), the Centers for Disease Control (CDC) and the Occupational Safety and Health Administration (OSHA). The primary sources were those available from the National Library of Medicine's Toxicology Data Network (ToxNet)[2].

Where this type of information was not available, or where more recent studies called into question the results previously published by authoritative bodies, supplementary information was noted. Differences of opinion among experts and variations in test results were also noted where applicable. Table 2.5.3 lists the environmental, health and safety parameters that were researched and evaluated. Specific sources of information for individual parameters are provided in the complete

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[1] Authoritative bodies include the US Environmental Protection Agency, the Occupational Safety and Health Administration, the National Toxicology Program, the International Agency on Research of Cancer, National Institute of Health, and the Centers for Disease Control, etc.

[2] Go to http://toxnet.nlm.nih.gov/ for more information

EH&S assessment tables in Appendix D. These sources also contain detailed background information about the parameters.

Unless otherwise noted in the tables in Appendix D, the assessments used the US EPA PBT Profiler[3] software to determine environmental persistence, bioaccumulation potential and toxicity for organic chemicals. The summary table for each use found within the individual chemical sections of this report includes the EH&S parameters judged to be most critical to the particular use and set of alternatives.

In many instances key parameter data were not available for all alternatives. In this case a "**?**" was inserted into the summary table. It is important for users of this report to consider the implication of data gaps for their particular situation. In some cases users may have access to data that the Institute did not, thereby allowing them to make a fuller comparison of the alternative to the reference chemical. In others, users can assume that a question mark is indicative of a need for additional research or testing.

Where appropriate the study also included readily available information on key life cycle considerations, such as waste disposal limitations, energy usage required during manufacture, impact on product recyclability or reuse potential, etc. This was typically included where complex materials or products were being assessed, rather than individual chemicals or formulations because the life cycle issues become more important in those types of comparisons. It is important to note that this study did not include comprehensive life cycle assessments of each alternative, but rather provides qualitative discussions of life cycle considerations where appropriate.

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[3] Go to http://www.pbtprofiler.net/ for more information

Table 2.5.3: EH&S Parameters Considered in Assessing Alternatives

Environmental Effects	Other Environmental Hazards	Acute Human Health Effects	Chronic Human Health Effects	Other Hazards
Hazardous Air Pollutant Water Solubility Density Specific Gravity Vapor Pressure Henry's Law Coefficient Kd (soil sorption coefficient) Koc (adsorption coefficient) Log Kow (octanol-water partition coefficient) Persistence: Water, Soil, Sediment, Air Bioaccumulation Aquatic Toxicity Drinking Water Quality	Degradation Products Ozone Depleting (ODC) Greenhouse Gas	Metabolites Dermal Absorption Lethal Dose concentration: Inhalation LC 50, Oral LD50, Dermal LD50 Occupational Exposure Limits: IDLH, PEL, REL, TLV, Ceiling/ST Irritation: Dermal, Ocular, Respiratory	Reference Dose Mutagenicity Carcinogenicity Skin Sensitization Reproductive & Developmental Toxicity Target Organ	Flammability Reactivity Corrosivity Flash Point

2.5.4 Procedures Followed for Evaluating Mixtures, Material Alternatives, and Process Alternatives

For the purposes of this study, a chemical is considered to be any element, chemical compound or mixture of elements and/or compounds. Chemicals are the constituents of materials. A chemical "mixture," also known as a chemical "preparation," includes multiple chemicals.

A one-for-one chemical substitution represents the simplest type of alternative, where the chemical being evaluated can be directly substituted with another chemical that satisfies the functional requirements for the particular use. In this instance, the alternatives assessment was relatively straightforward; information associated with the parameters in Appendix A were obtained, verified and presented in a way that allows a direct comparison of the two chemicals.

Evaluating Mixtures

Often the chemicals being evaluated are used in formulations of multiple chemicals. In this case, each of the chemical constituents of the mixture was considered in the assessment in a manner similar to that used for individual chemicals (as above). The Institute obtained environmental and human health information about each of the chemical constituents of a mixture, and performance and cost information for the overall formulation when doing the assessment. The primary source of information on the constituents of a mixture was the product Material Safety Data Sheet (MSDS).

For the purposes of this study, the Institute focused on the primary constituents of each formulation being evaluated. Specifically, constituents present in amounts exceeding 1% by mass were included in the assessment. Although no quantitative indicators were calculated for mixtures during the evaluation process, the general approach was to consider the weight percents of constituent chemicals in determining overall EH&S impacts. When formulation breakdowns were presented on associated MSDSs as a range, the Institute assumed the average weight percentage of the range presented.

As the EH&S factors associated with the constituents of a mixture were determined, their relative significance to the overall EH&S characteristic of the mixture was evaluated based on the weight percent within the mixture. The actual approach to evaluating the EH&S impact of a mixture differed depending on whether the chemicals in the mixture cause similar or different health effects. If the health effects are similar (*e.g.,* two constituents are central nervous system (CNS) depressants), their weight percentages were added and the overall impacts of the combined chemicals assessed. If the health effects are different (*e.g.,* one chemical is a CNS depressant, while another is a respiratory irritant), the effects were evaluated separately based on the weight percentages of each constituent.[4]

When alternative mixtures were evaluated in summary tables, an attempt was made to apply the weighting criteria described above, although the resulting indicator typically reflected the most problematic constituent for that mixture.

Evaluating Material Alternatives

A material is defined as the basic matter (*e.g.,* metal, wood, plastic, fiber) from which the whole or the greater part of something physical (*e.g.,* a machine, tool, building, fabric) is made. In some cases the chemical being studied is used to impart particular qualities in a material. For instance, DEHP is used in poly vinyl chloride (PVC) to make this otherwise rigid plastic flexible. Rather than find other ways to make the material (PVC) less rigid, there may be opportunities to find alternative materials (*e.g.,* other plastics) that are inherently more flexible, therefore bypassing the need for this particular chemical additive.

When evaluating material alternatives, performance and cost considerations may be readily compared. However the impact of a material on environmental or human health may not be as readily assessed as it can be for chemical substitutes. For materials, life cycle considerations may become more important. For this study the Institute looked both at EH&S impacts when appropriate and at life cycle issues that, based on the research, appear to be of most significance relative to the material being replaced. The inclusion of life cycle considerations only occurred when a preponderance of literature indicated that life cycle issues exist that should be accounted for. It is important to note that comprehensive life cycle assessments were not performed as part of this study. Rather, when the research indicated that at a particular point in a material's life cycle there are important positive or negative impacts, these were noted qualitatively relative to the material being substituted.

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[4] This approach to mixtures is widely used in occupational and environmental health. See e.g. Craig, et al., "Recommended Default Methodology for Analysis of Airborne Exposures to Mixtures of Chemicals in Emergencies," Ann Occ Env Hyg 14 (9): 609-17, 1999.

Evaluating Process Alternatives

For the purposes of this study, process alternatives are those that employ a different technology, process or approach to achieve the objective or function of the original product or process associated with the chemical. For example, when considering alternatives to perchloroethylene in vapor degreasing, one approach might be to change the upstream process to use lubricants that either do not require cleaning, or are easier to remove using water-based surfactants.

The feasibility of this type of alternative can be assessed, but it is very difficult to compare the EH&S impacts quantitatively. These types of alternatives are included in the study where appropriate, and their feasibility assessed qualitatively. Where our research indicates that there are important positive or negative attributes or impacts relative to the substance being substituted, these are mentioned.

2.6 Economic Impact Study

As part of the study, the Commonwealth requested an analysis of potential impacts on employment level and economic competitiveness of the Commonwealth from adopting any alternative chemical or technology. Dependable economic and employment predictions are lengthy and expensive to prepare, and require a great deal of information about both broad economic conditions and material and industry-specific costs. In addition, the impacts cannot be generalized across products and industry sectors. Rather, the impacts depend on the many different situations that exist for the five chemicals, their uses and alternatives.

Therefore, the approach taken in this study was to develop guidance to those seeking to quantify economic impacts from substitution by identifying the principal factors that influence the result for a given situation. Case material was used to create a useful list of economic factors present in particular situations. Further development by experts of the influences, duration, dynamics, interactions, sector specificity or other characteristic of these economic factors led to useful guidance regarding economic impacts for specific alternatives.

This evaluation was completed using the following process:

1. The Institute briefly reviewed existing literature on the economic impact of environmental regulations, alternatives assessment and the TURA program.
2. Case materials were created for the following sectors: formaldehyde in building materials, lead in electronics, and perchloroethylene in dry cleaning. This material was used to focus the discussion by experts. (See Appendix E)
3. Ten experts in the economics of technology change and innovation were gathered for a facilitated discussion. They included representatives from Associated Industries of Massachusetts, the Small Business Association, the Massachusetts Manufacturing Partnership, Tufts University, Northeastern University, the University of Massachusetts, the Economic Development Research Group, Tellus Institute, and the Environmental Management Accounting Research and Information Center. Using the case materials, a list of economic factors and their influences was developed.

Chapter 8 presents a summary of this analysis and a framework outlining the factors that may influence the economic impact of adopting an alternative chemical or technology. Due to the limitations discussed above, this chapter does not present specific quantitative information.

2.7 Quality Assurance/Quality Control (QA/QC)

All EH&S data were initially collected by one Institute staff member and independently verified by a second staff member. The initial data were entered into a spreadsheet; this included the chemical name and CAS number, the actual data, and the sources of the data. The second staff member independently checked the accuracy of the CAS number and consulted the original data source and, where available, a secondary source. If data sources were inconsistent, the information was further evaluated and either a determination was reached or the differences noted. Each Institute researcher leading the individual chemical assessment section also reviewed the data provided, and augmented the EH&S data using current peer-reviewed scientific research obtained during the course of the assessment.

In addition to general input on the methodology for this study that was received from stakeholders and experts, the Massachusetts Toxics Use Reduction Act Science Advisory Board (SAB) was asked to review the screening criteria and environmental, health and safety parameter list. The SAB was created by the Toxics Use Reduction Act (TURA) of 1989 specifically to advise the Institute on scientific matters, and consists of experts in health and environmental issues, as well as technical chemical experts. They commented on the draft methodology and concurred with the final methodology.

Each assessment was sent out to the appropriate stakeholders and experts for general technical review. Reviewers provided a great deal of valuable technical feedback that improved the accuracy of the study, but were not asked to verify all information and data in the report.

Chapter 3. Lead and Lead Compounds

Five Chemicals Alternatives Assessment Study

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3.1 Lead Overview

3.1.1 Characteristics of Lead

Lead is a natural, bluish-gray metal. The chemical formula for lead is Pb, and its atomic weight is 207.2 g/mol. The Chemical Abstract Series number for lead is 7439-92-1. (National Institute for Occupational Safety and Health 2004) The following table provides a summary for key chemical and physical characteristics for lead.

Table 3.1.1 Lead Summary Table

Chemical and Physical Characteristics of Lead (*2*)	
Melting/Boiling Point	327.4° C / 1,740° C
Vapor Pressure	1.77 mm Hg at 1,000° C
Octanol/Water Partition Coefficient	No data for Log Kow
Density	11.34 g/cm^3
Solubility in Water	Pure lead is insoluble, lead compounds may vary from insoluble to soluble
Soil Sorption Coefficient	No data for Log Koc
Solubility in Organic Solvents	Insoluble
Henry's Law Coefficient	No data

Manufacturers use lead in the form of a metal for many different products. Lead possesses the general physical properties of other metals as a conductor of electricity and heat. Lead has low melting temperature (327° C) and extreme malleability, which enables the easy casting, shaping, and joining of lead products. Lead is relatively abundant in the earth, and has a fairly low price when compared with other non-ferrous metals. Lead can be recycled as a secondary raw material from lead-acid batteries and other lead products (Thornton, et al. 2001).

The high density of lead is desirable for several product categories including weighting applications, and shielding against sound, vibration, and radiation. However, lead has very low tensile strength which precludes its use for applications that require even moderate strength. Creep is the slow plastic deformation of materials under a constant stress. Lead is subject to creep at normal temperatures because its melting temperature is relatively low (Thornton, et al. 2001).

Lead is commonly used in various alloys which offer physical properties different than elemental lead. For example, the strength and creep resistance for lead can be improved with the small additions of other metals (e.g. copper) to form alloys with more desirable mechanical properties.

Lead compounds have different physical properties than elemental lead, and are used for various products. The NLM HSDB lists over 120 lead compounds. The major lead compounds used in commerce are lead oxide (PbO), lead tetraoxide (Pb_3O_4), basic lead carbonate (white lead), tribasic lead sulfate, and dibasic lead phthalate. For example, the reactions of lead oxide in dilute sulfuric acid are fundamental to the operation of a lead-acid battery.

3.1.2 Potential Health and Environmental Impacts of Lead

Summary

Lead is used in the manufacture of batteries, metal products, cables, ceramic glazes, and other various products. Exposure to lead can occur from breathing contaminated workplace air or house dust or ingesting lead-based paint chips or contaminated dirt. Lead is a very toxic element, causing a variety of effects at low dose levels. Brain damage, kidney damage, and gastrointestinal distress are seen from acute (short-term) exposure to high levels of lead in humans. Chronic (long-term) exposure to lead in humans results in effects on the blood, central nervous system (CNS), blood pressure, kidneys, and Vitamin D metabolism. Children are particularly sensitive to the chronic effects of lead, with slowed cognitive development, reduced growth and other effects reported. Reproductive effects, such as decreased sperm count and spontaneous abortions, have been associated with high lead exposure. The developing fetus is at particular risk from maternal lead exposure, with low birth weight and slowed postnatal neurobehavioral development noted. Human studies are inconclusive regarding lead exposure and cancer.

Hazards

Human exposure to lead occurs through a combination of inhalation and oral exposure, while dermal absorption of inorganic lead compounds is reported to be much less significant than absorption by inhalation or oral routes. Inhalation generally contributes a greater proportion of the dose for occupationally exposed groups, and the oral route generally contributes a greater proportion of the dose for the general population. The effects of lead are the same regardless of the route of exposure (inhalation or oral) and are correlated with internal exposure, as blood lead levels. For this reason, this report will not discuss the exposure in terms of route but will present it in terms of blood lead levels.

Acute (Short-Term) Health Effects

Death from lead poisoning is likely to occur in children who have blood lead levels greater than 125 μg/dL and brain and kidney damage have been reported at blood lead levels of approximately 100 μg/dL in adults and 80 μg/dL in children. Gastrointestinal symptoms, such as colic, have also been noted in acute exposures at blood lead levels of approximately 60 μg/dL in adults and children. Short-term (acute) animal tests in rats have shown lead to have moderate to high acute toxicity. (Agency for Toxics Substances and Disease registry (ATSDR) 1999). Effects on glomeral filtration, neurodevelopment, and blood pressure are evident are blood lead levels below 10 μg/dL. The most sensitive targets for the toxic effects of lead are the kidneys and the hematological, cardiovascular, and nervous systems. Because of the multi-modes of action of lead in biological systems, lead could potentially affect any system or organ in the body (ATSDR 2005).

Chronic (Long-Term) Health Effects

Non-cancer Effects

Chronic exposure to lead in humans can affect the blood. Anemia has been reported in adults at blood lead levels of 50 to 80 μg/dL, and in children at blood lead levels of 40 to 70 μg/dL. Lead also affects the nervous system. Neurological symptoms have been reported in workers with blood lead levels of 40 to 60 μg/dL, and slowed nerve conduction in peripheral nerves in adults occurs at blood lead levels of 30 to 40 μg/dL. Children are particularly sensitive to the neurotoxic effects of lead. There is evidence that blood lead levels of 10 to 30 μg/dL, or lower, may affect the hearing threshold and growth and development in children (ATSDR 1999). Meta-analyses conducted on cross-sectional and prospective studies suggest and IQ decline of 1 – 5 points is associated with an increase in lead blood level of 10 μg/dL. No threshold for the effects of lead on IQ has been identified.

Other effects from chronic lead exposure in humans include effects on blood pressure and kidney function, and interference with vitamin D metabolism. Animal studies have reported effects similar to those found in humans, with effects on the blood, kidneys, and nervous, immune, and cardiovascular systems noted.

The U.S. Environmental Protection Agency (EPA) has not established a Reference Concentration (RfC) or a Reference Dose (RfD) for elemental lead or inorganic lead compounds. EPA has established a Reference Dose for tetraethyl lead (an organometallic form of lead) of 1×10^{-7} milligrams per kilogram body weight per day (mg/kg/d) based on effects in the liver and thymus of rats.

Cancer Risk

Human studies are inconclusive regarding lead exposure and an increased cancer risk. Four major human studies of workers exposed to lead have been carried out; two studies did not find an association between lead exposure and cancer, one study found an increased incidence of respiratory tract and kidney cancers, and the fourth study found excesses for lung and stomach cancers. However, all of these studies are limited in usefulness because the route(s) of exposure and levels of lead to which the workers were exposed were not reported. In addition, exposure to other chemicals probably occurred. Animal studies have reported kidney tumors in rats and mice exposed to lead via the oral route. EPA considers lead to be a Group B2, probable human carcinogen. International Agency for Research on Cancer (IARC) considers inorganic lead compounds to be probably carcinogenic to humans (Group 2A), and organic lead compounds to be not classifiable as to their carcinogenicity to humans (Group 3).

Reproductive/Developmental Effects

Studies on male lead workers have reported severe depression of sperm count and decreased function of the prostate and/or seminal vesicles at blood lead levels of 40 to 50 μg/dL. These effects may be seen from acute as well as chronic exposures. Occupational exposure to high levels of lead has been associated with a high likelihood of spontaneous abortion in pregnant women. However, the lowest blood lead levels at which this occurs has not been established. These effects may also be seen from acute as well as chronic exposures. Exposure to lead during pregnancy produces toxic effects on the human fetus, including increased risk of preterm delivery, low birthweight, and impaired mental development. These effects have been noted at maternal blood lead levels of 10 to 15 μg/dL, and possibly lower. Decreased IQ scores have been noted in children at blood lead levels of approximately 10 to 50 μg/dL (ATSDR 1999).

Human studies are inconclusive regarding the association between lead exposure and other birth defects, while animal studies have shown a relationship between high lead exposure and birth defects.

Environmental Hazards

Lead is a naturally occurring, bluish-gray metal that is found in small quantities in the earth's crust. Lead is present in a variety of compounds such as lead acetate, lead chloride, lead chromate, lead nitrate, and lead oxide. Lead readily tarnishes in the atmosphere but it is one of the most stable fabricated metals because of its corrosive resistance to air, water, and soil. Pure lead is insoluble in water; however, the lead compounds vary in solubility from insoluble to water soluble. The vapor pressure for lead is 1.00 mm Hg at 980° C (National Institute for Occupational Safety and Health 2004).

Lead particles are removed from the atmosphere by wet and dry deposition. The average residence time in the atmosphere is ten days, during which long distance transport up to thousands of kilometers may take place. Lead is extremely persistent in both water and soil. The presence of lead in these media varies widely depending on such factors as temperature, pH, and the presence of humic materials.

Although combustion of leaded gasoline was one the primary source of anthropogenic atmospheric releases of lead, industrial releases from smelters, battery plants, chemical plants, and disturbance of older structures containing lead based paints are now major contributors to total lead releases.

Biologists have studied the effects of lead sinkers and jigs on waterbirds, such as loons and swans, since the 1970s. A single fishing sinker swallowed with food or taken up as grit could be fatal to waterbirds. Lead adversely affects the function and structure of the kidney, central nervous system, bones, and production and development of blood cells in waterbirds. Exposure to lead, such as through ingestion of fishing sinkers, can cause lead poisoning in waterbirds, producing convulsions, coma, and death (USEPA 1994).

Exposure Routes

Worker Health

The primary use of lead in the U.S. is in the manufacture of batteries. Lead is also used in the production of metal products, such as sheet lead, solder (but no longer in food cans), and pipes, and in ceramic glazes, paint, ammunition, cable covering, and other products.

Potentially high levels of lead occur in the following industries: primary and secondary lead smelting and refining industries, steel welding or cutting operations, battery manufacturing plants, construction, rubber products and plastics industries, printing industries, firing ranges, radiator repair shops, and other industries requiring flame soldering of lead solder. In these work areas, the major routes of lead exposure are inhalation and ingestion of lead-bearing dusts. In the smelting and refining of lead, mean concentrations of lead in air can reach 4,470 $\mu g/m^3$; in the manufacture of storage batteries mean airborne concentrations of lead from 50 to 5,400 $\mu g/m^3$ have been recorded. (ATSDR 1999) The following bullets include various occupational threshold limits:

- The NIOSH REL for an 8 – 10 hour time-weighted-average exposure is 0.10 mg/m^3 (IARC 2004).
- The NIOSH IDLH is 100 mg/m^3 ((IARC 2004).
- The OSHA PEL for an 8 hour work day is 0.5 mg/m^3 (Smith 2003).
- The ACGIH TLV is 0.5 mg/m3 over an 8 hour workshift (Smith 2003).

Public Health

This section lists the major exposures of lead to the public, but is not intended to be an exhaustive listing of all potential exposures. The largest source of lead in the atmosphere has been from leaded gasoline combustion, but with the phase out of lead in automotive gasoline, air lead levels have decreased considerably. Other airborne sources include combustion of solid waste, coal, and oils, emissions from iron and steel production and lead smelters, general aviation aircraft, racing vehicle, marine fuels, and tobacco smoke.

Exposure of the general population to lead is most likely to occur through the ingestion of contaminated food and drinking water, and by the inhalation of lead particulates in ambient air. Fruits, vegetables, and grains may contain levels of lead in excess of background levels as a result of plant uptake of lead from soils and direct deposition of lead onto plant surfaces. Common source of exposure for children is lead-based paint that has deteriorated into paint chips and lead dusts, and common sources of lead exposure for adults include occupational and non-occupational such as do-it-yourself paint scraping, renovations, and castings. For example, using heat guns or dry scraping of old lead containing paint during home reconstruction and remodeling can result in lead exposure.

Exposure to lead can also occur from food and soil. Children are at particular risk to lead exposure since they commonly put hands, toys, and other items in their mouths, which may come in contact with lead-containing dust and dirt. Lead-based paints were commonly used until 1978 and flaking paint, paint chips, and weathered paint powder may be a major source of lead exposure, particularly for children. Children are also exposed by handling lead-stabilized PVC plastics and lead alloy jewelry and toys. Lead in drinking water is due primarily to the presence of lead in certain pipes, solder, and fixtures (i.e. brass fixtures).

Lead exposure to the general public can also occur during the use of inadequately glazed or heavily worn earthenware vessels for food storage and cooking, as well as by engaging in certain hobbies such as using recreational shooting ranges, stained glass making, or using molten lead in casting ammunition, fishing weights, or toy figurines.

Lead has been listed as a pollutant of concern to EPA's Great Waters Program due to its persistence in the environment, potential to bioaccumulate, and toxicity to humans and the environment. The National Ambient Air Quality Standard (NAAQS) are set by the U.S. EPA for pollutants that are considered to be harmful to public health and the environment. The NAAQS for lead is 1.5 $\mu g/m^3$, which is the maximum arithmetic mean averaged over a calendar quarter (New Jersey Department of Health and Senior Services 2001).

3.1.3 Use and Functionality

The various physical properties of lead were outlined in Section 5.1.1. Lead may be used in the form of metal, alloyed with other metals, or as chemical compounds. The commercial importance of lead is based on its ease of casting, high density, low melting point, low strength, ease of fabrication, acid resistance, electrochemical reaction with sulfuric acid, and chemical stability in air, water, and soil. Many of the physical properties of lead are desirable for various product categories such as storage batteries, ammunition, casting materials, and sheet lead. The total global consumption of lead in 2003 was estimated to be 15.1 billion pounds, and the U.S. consumption of lead in 2003 was estimated to be 3.06 billion pounds. The greatest use of lead is in lead-acid batteries, however lead-acid batteries are not manufactured in Massachusetts (USEPA 1999).

3.2 Lead Use Identification and Prioritization

3.2.1 Use Identification

Lead has many desirable material properties and has a variety of uses. A summary of the major uses is provided below. (Please see Appendix B for a more detailed description of the various uses of lead).

- Batteries
- Ammunition
- Glass
- Heat Stabilizer in Plastics & Resins
- Metal Finishing
- Electronics (solder, board surface finish, components)
- Sheet Lead (sound barriers, roof flashing, radiation shielding)
- Bulk Metal (castings, weighting applications, ammunition)
- Pigments

In order to determine which uses were a priority for assessment in Massachusetts, the following criteria were evaluated:

1. Importance to the Commonwealth of Massachusetts:
    - Use in manufacturing: Total quantity of chemical used in manufacturing operations in Massachusetts
    - Use in consumer products: Total quantity of chemical used in products sold in Massachusetts.
2. Potential availability of alternatives.
3. Exposure potential (environmental, occupational, and public health).
4. Potential value to Massachusetts businesses and citizens of the alternatives assessment results. Specifically, the preferences of the pertinent stakeholders for each chemical were given priority. This stakeholder input was provided during a stakeholder meeting held during October 2006, and from a stakeholder input survey.

<u>Uses in Products</u>

The following table illustrates the uses of lead in various products:

Table 3.2 A: Uses of Lead

Use	U.S. Consumption in 2003 (Pounds)	Percentage of Total U.S. Consumption
Storage batteries	2,578,680,000	84.2%
Ammunition	107,555,200	3.5%
Miscellaneous Uses	93,890,400	3.1%
Oxides	78,682,800	2.6%

Table 3.2 A: Uses of Lead		
Use	**U.S. Consumption in 2003 (Pounds)**	**Percentage of Total U.S. Consumption**
Casting metals	69,866,800	2.3%
Sheet lead	53,336,800	1.7%
Other metal products	50,251,200	1.6%
Solder	13,907,240	0.5%
Proprietary corporate data	6,620,816	0.2%
Billets, ingots	6,193,240	0.2%
Extruded products	3,680,680	0.1%
Bearing metals	894,824	0.0%
Totals:	3,063,560,000	100.0%
Source: USGS		

Use in Massachusetts Manufacturing/Operations

The following table illustrates the uses of lead in various manufacturing and operations in Massachusetts. This table includes lead use as reported by Massachusetts facilities covered by the Toxics Use Reduction Act (TURA). This is not an exhaustive list because it does not include facilities with less than ten employees, facilities with SIC codes not covered by TURA, and facilities using less than TURA defined threshold amounts.

Table 3.2 B: Use of Lead in Massachusetts			
Major Use Category	**TURA Total Use (2003)**	**Pounds**	**Number of Filers**
PVC/Rubber	42.4%	3,955,938	39
Waste Combustors	28.3%	2,642,987	4
Waste Management	14.9%	1,395,219	4
Pigments	2.3%	211,596	4
Metal Finishing	2.2%	201,130	14
Casting/Extrusion	2.0%	190,223	17
Electronics	2.0%	186,434	59
Glass	1.7%	162,137	10
Sheet Lead	1.7%	157,197	3
Power Generation	1.3%	122,861	7
Ceramics	0.6%	58,212	3

Table 3.2 B: Use of Lead in Massachusetts			
Major Use Category	**TURA Total Use (2003)**	**Pounds**	**Number of Filers**
Miscellaneous	0.3%	28,490	40
Ammunition	0.1%	13,782	1
Concrete/Stone	0.1%	10,564	19
Batteries	0.0%	0	0
Totals:	100.0%	9,336,770	224

Source: TURA Data, 2003

Lead Releases in Massachusetts

The following table illustrates the releases of lead in Massachusetts. This table is not an exhaustive listing of releases because it is limited to the generators covered under the U.S. EPA Toxics Release Inventory program.

Table 3.2 C: Lead Released in Massachusetts			
Major Use Category	**TRI Releases in MA (2003)**	**Pounds**	**Number of Filers**
Waste Management	49.4%	140,468	2
PVC/Rubber	25.4%	72,025	21
Glass	7.8%	22,033	9
Power Generation	7.8%	22,289	6
Ammunition	4.0%	11,414	1
Miscellaneous	1.5%	4,236	36
Electronics	1.3%	3,733	39
Casting/Extrusion	1.0%	2,854	10
Metal Finishing	0.9%	2,426	10
Concrete/Stone	0.5%	1,282	5
Ceramics	0.3%	825	3
Pigments	0.2%	495	3
Sheet Lead	0.0%	5	1
Batteries	0.0%	0	0
Waste Combustors	0.0%	0	0
Totals:	100.1%	284,085	146
Source: U.S. EPA TRI Data, 2003			

Summary of Stakeholder Input

Stakeholder participation at the October 2005 and November 2005 stakeholder meetings included Massachusetts representatives from industry, government, and environmental organizations. The following considerations were evaluated during the prioritization process for the major uses of lead.

Batteries:

- Highest level of lead use accounting for approximately 84% of all lead use in the United States.
- In general, there is a good infrastructure in place for recycling lead in batteries at product end of life.
- Many available battery alternatives contain nickel, cadmium, or other toxic materials.
- Most safer battery alternative technologies are still emerging.

Electronics

- Broad use in Massachusetts by approximately 59 facilities in the electronics industry. However, only a small quantity of lead is incorporated into the product.
- The European Union's directive called Restriction of the use of certain Hazardous Substances (RoHS) restricts the use of lead in many electronics applications. This directive has initiated a movement toward lead-free electronics for affected electronics companies in Massachusetts.
- The electronics industry has already moved toward a standard alternative for lead solder. This alternative is an alloy consisting of tin, copper, and silver (SAC alloy). The Institute has been involved with the electronics industry researching, testing, and evaluating this lead-free alloy for electronics assembly for the past five years.
- The U.S. EPA Design for Environment project has recently completed a comprehensive life cycle analysis for lead and lead-free solders. Therefore, by undertaking an alternatives assessment for lead solder we wouldn't be adding much value to decision making by companies.

Sheet Lead

- Sheet lead is used mostly for roof flashing and radiation shielding applications.
- Lead works well for radiation shielding. For this use, the lead is often isolated from exposure during use and the lead is also easily recyclable.
- There are many commercially available alternatives for lead roof flashing.
- There were health concerns for construction workers and home owners using lead roof flashing.
- Lead use in roof flashing was considered to be added to the priority list if additional time and resources were made available in 2006.

Heat Stabilizers in PVC and Elastomers

- The largest use in Massachusetts manufacturing, accounting for 42% of lead use. Thirty-nine manufacturing facilities in Massachusetts reported a total of approximately 4 million pounds in 2003.
- Many lead-free heat stabilizers are commercially available, and companies are adopting alternative heat stabilizers.

- The U.S. EPA Design for Environment project is underway to evaluate three specific wire/cable applications. In the longer term, this effort will provide life cycle assessment information for several heat stabilizer alternatives.
- There is little or no recycling at end of life for PVC products containing lead.
- An overview of the current market situation for lead-free heat stabilizers would provide high value to Massachusetts manufacturers. There is value to understanding in the short term the various alternatives available before substitutions are made. Wire and cable is an excellent example of lead heat stabilizers used in PVC products.

Weight Applications: Wheel Weights

- Wheel weights commonly become detached from automobile wheels and end up in the environment.
- Several alternatives are in use and are commercially available.
- The Ecology Center of Ann Arbor, Michigan has already gathered some wheel weight information that will be valuable for conducting an alternatives assessment.
- Worker exposure is a concern during installation of wheel weights for new automobiles as well as during after market installation.
- Wheel weights are a good example of lead used in weighting applications. Conducting an alternatives assessment in this area will provide high value to address worker exposure and environmental concerns.

Weight Applications: Fishing Sinkers

- Several states in the Northeast have banned the use of certain lead sinkers. Massachusetts still allows the use of lead fishing sinkers except for use in the Quabbin and Wachusett Reservoirs.
- Several lead-free alternatives are in use and are commercially available.
- Fishing sinkers of all types are lost during use. These fishing sinkers end up in the environment and some of these lead sinkers are ingested by waterfowl.
- Thousands of anglers in the U.S. produce their own lead fishing sinkers.
- Fishing sinkers are a good example of lead used in weighting applications. Conducting an alternatives assessment in this area will provide high value to address wildlife and environmental concerns, as well as health concerns during production and use of lead sinkers by individual anglers.

Ammunition for Shooting Ranges

- Second highest use of lead, accounting for approximately 4% of lead use in the United States.
- For outdoor shooting ranges in Massachusetts, the lead in ammunition usually ends up in the environment and often leads to soil and/or sediment contamination and potentially surface water and groundwater contamination. .
- For indoor shooting ranges, there is high worker and shooter exposure to lead.

- Several alternatives are in use and are commercially available.
- There is a Massachusetts manufacturer of firearms that uses lead ammunition for testing purposes.
- Conducting an alternatives assessment in this area will provide high value to shooting range workers, shooting enthusiasts and public safety personnel.

Pigments

- Most uses of lead pigments have been phased out.
- Lead pigments are primarily used for traffic paint in Massachusetts.
- The single Massachusetts manufacturer of traffic paint is transitioning to a lead-free alternative.
- Lead use in pigments was considered to be added to the priority list if additional time and resources were available.

Castings/Extrusion (jewelry, ornamental, etc.)

- There are 17 TURA filers in Massachusetts that used approximately 190,000 pounds of lead in 2003.
- There is a potentially high consumer exposure during use, especially in children's jewelry.
- Most children's jewelry is now imported, so there is limited control on material selection for foreign manufacturers.
- There are some alternatives commercially available.

In addition to the stakeholder meeting, a survey was provided to stakeholders to solicit their input to prioritize the various uses of lead. Four stakeholders completed and returned this survey. In general, the stakeholder input for the various uses of lead fell into one of the following three categories outlined in the following table:

Table 3.2 D: Stakeholder Input

Stakeholder Input	Lead Use
One or more stakeholders considered this use a low priority	Batteries, Glass, Metal Finishing, Electronics
Stakeholders either did not rank this use or considered it a medium priority	Sheet lead
Stakeholders indicated this use was either a medium or high priority (with at least two stakeholders considered this a high priority)	Heat stabilizers, weight applications, ammunition, pigments

3.2.2 Use Prioritization

Based upon applying the criteria discussed above, the following three applications were selected as priority lead uses for this alternatives assessment project: In summary, these applications were chosen based on stakeholder input, importance to Massachusetts industry and consumers, and likely availability of alternatives. Ammunition when used at indoor and outdoor firing ranges was thought to be a significant source of lead contamination in the Commonwealth. Wheel weights and fishing to be a significant source of lead contamination in the Commonwealth. Wheel weights and fishing sinkers were chosen to be representative of a large number of lead uses that rely on its high density. Wire and cable heat stabilization is the category with the largest use of lead among Massachusetts manufacturers. The priority uses of lead that will be studied are:

- Ammunition for shooting ranges;
- Weighting applications (wheel weights and fishing sinkers);
- Heat stabilizers used in PVC wire and cable coatings.

3.3 Lead Alternatives Identification and Prioritization

Since there are so many alternatives for the various uses of lead, the Institute was not able to fully evaluate them all in the short time span allowed for this project. Therefore, the Institute conducted an evaluation to determine those alternatives that are most feasible based upon the following criteria:

- ***Performance***: Known performance of alternative compared to that of the hazardous chemical. Consider the potential for future performance enhancements (e.g. research funds available for further product development).
- ***Availability***: Number of suppliers/manufacturers that commercially provide the alternative.
- ***Manufacturing Location***: Is the product manufactured in Massachusetts or outside of Massachusetts.
- ***Cost***: Current costs associated with the alternative compared to that of the hazardous chemical. Consider the potential for future cost reductions (*e.g.,* economies of scale due to higher volume production).
- ***Environmental, Health, and Safety***: Known environmental, health and safety risks compared to that of the hazardous chemical.
- ***Global Market Effect***: Information about pending or existing global restrictions that might materially affect the ability of an industry to market its products internationally.
- ***Stakeholder Value***: Stakeholders placing a high priority on a particular alternative so as to inform their decisions.

3.3.1 Alternatives Associated with Ammunition for Shooting Ranges

Available Alternatives

Alternatives based on the following substances were identified:

- Bismuth
- Copper
- Iron
- Tungsten
- Zinc
- Brass
- Bronze
- Ceramic
- Plastic/polymeric
- Steel
- Tin
- Beryllium

Alternatives Screening

Beryllium and beryllium compounds: The U.S. Department of Health and Human Services and the International Agency for Research on Cancer have determined that beryllium and beryllium compounds are human carcinogens. EPA has determined that beryllium is a probable human carcinogen.

Alternatives Prioritization

A law passed in 1986 makes it unlawful to manufacture or import armor-piercing ammunition, which eliminates the possibility of producing handgun ammunition using tungsten alloys, steel, iron, brass, bronze, beryllium copper, or depleted uranium, unless the projectiles are frangible (break apart into small pieces on contact with any hard surface) and are intended for target shooting applications.

Bismuth

Bismuth is similar to lead in density and softness and therefore has the advantage of having ballistic performance which is similar to lead. At least one major ammunition manufacturer produces bismuth handgun bullets. Bismuth is used to produce frangible bullets by plating a cast bismuth core with a copper jacket, or by mixing bismuth with other materials including polyethylene or zinc. Preliminary research indicates that bismuth is a less toxic alternative to lead for use in handgun ammunition used at indoor firing ranges. In January of 1997, bismuth-tin shotgun shot was granted full approval by the U.S. Fish and Wildlife Service as an alternative to lead shotgun shot for hunting migratory waterfowl.

Copper

Copper is widely used as a jacket material for both lead and lead-free bullets. Copper powder is also used to produce frangible bullets, typically in a mixture with other powdered metals including tin, iron, or tungsten. Copper has a density of 8.9 g/cm^3 which is 22% less than lead and will result in either lighter bullets or increased bullet size.

Several major ammunition manufacturers use copper and/or copper powder to produce lead-free handgun ammunition. The cost of copper is roughly 3.5 times the cost of lead. Frangible handgun ammunition made with sintered (heated without melting to form a coherent mass) copper powder is significantly more expensive than lead ammunition but it is competitive with other types of frangible ammunition or reduced hazard ammunition.

Iron

Iron powder has successfully been used to produce frangible handgun bullets. Iron has a density of approximately 7.6 g/cm^3 which is 32% less than lead and will result in either lighter bullets or increased bullet size. Iron handgun bullets, excluding frangible bullets, are banned because they are considered to be armor piercing ammunition. Frangible handgun ammunition made with iron powder is significantly more expensive than lead ammunition but it is competitive with other types of frangible ammunition or reduced hazard ammunition. Iron has the advantage of being magnetic which could facilitate recovery for recycling.

Tungsten

Tungsten has a density of 19.25 g/cm^3 which is 1.7 times the density of lead. Tungsten ammunition can be produced to provide similar ballistic performance to lead ammunition. Several major ammunition manufacturers produce lead-free frangible ammunition using tungsten. Tungsten alloy handgun bullets, excluding frangible bullets, are banned because they are considered to be armor piercing ammunition.

Frangible handgun ammunition made with tungsten is significantly more expensive than lead ammunition but it is competitive with other types of frangible ammunition or reduced hazard ammunition. In January of 1997, several types of tungsten shotgun shot were granted full approval by the U.S. Fish and Wildlife Service as alternatives to lead shotgun shot for hunting migratory waterfowl.

Zinc

Zinc has a density of 7.05 g/cm^3 which is 62% of the density of lead will result in either lighter bullets or increased bullet size. Zinc can be used to produce frangible bullets either by forming the bullets out of zinc powder or zinc wire. Considering commodity prices of metals, zinc is one of the least expensive alternatives to lead. It is approximately twice the cost of lead.

Based on the previously listed criteria, alternatives based on the following materials were given a lower priority for assessment

1. Brass: Brass handgun bullets, excluding frangible bullets, are banned because they are considered to be armor piercing ammunition. Based on internet searches of ammunition manufacturers' and dealers' websites, brass frangible handgun bullets do not appear to be available in the commercial marketplace.
2. Bronze: Bronze handgun bullets, excluding frangible bullets, are banned because they are considered to be armor piercing ammunition. Based on internet searches of ammunition manufacturers' and dealers' websites, bronze frangible handgun bullets do not appear to be available in the commercial marketplace.
3. Ceramic: Ceramic bullets are significantly lighter than lead bullets which results in differences in ballistic performance. Ceramic bullets are used in some training applications where frangible bullets are required but, according to Richard Patterson (SAAMI), ceramic bullets are not widely accepted as a substitute for lead handgun bullets because the low density of ceramic negatively impacts performance.
4. Plastic: Molded plastic bullets are available for limited target practice. These reusable lightweight handgun bullets use primer power alone (no powder load) and therefore have velocities of only 300-400 feet per second and a range of only 25 feet. Since they do not utilize a powder load there is no recoil and the ballistic performance is significantly different from lead bullets.
5. Steel: Steel handgun bullets are banned because they are considered to be armor piercing ammunition. Based on internet searches of ammunition manufacturers' and dealers' websites, steel frangible handgun bullets do not appear to be available in the commercial marketplace.
6. Tin: Tin is used as a minor component in several types of bullets including lead, tungsten, and copper bullets. One major manufacturer produces ammunition with a tin core and copper jacket. Several of the alternatives that contain tin are included in the assessment but are included under the primary materials such as copper and tungsten.

High Priority Ammunition for Shooting Ranges Alternatives

The following alternative ammunitions were selected for assessment:

- Bismuth
- Copper
- Iron
- Tungsten
- Zinc

3.3.2 Alternatives Associated with Wheel Weights

Available Alternatives

The following were identified as potential alternatives to lead wheel weights:

- Zinc and ZAMAC (an alloy of zinc, aluminum and copper)
- Steel
- Plastic
- Copper
- Steel
- Tin
- Tungsten
- Iron
- Internal balancing systems, including plastic beads or other material inserted into the tire

Several European and Japanese automobile manufacturers have already switched to zinc or steel wheel weights. While auto manufacturers are making some progress to switch to lead-free wheel weights, the Institute noted that 80% of wheel weights are used by aftermarket businesses such as tire retailers and service stations and very few of these businesses use lead-free wheel weights.

Alternatives Prioritization

Alternatives that appeared likely to meet the following performance criteria were given a higher priority for assessment:

- Should meet automotive industry standards and specifications established for lead wheel weights
- Should be made of a dense material to minimize size
- Should be corrosion resistant
- Should be resistant to high temperatures
- Should be recyclable

Copper

Copper has several properties that match the requirements of wheel weight applications. It is relatively dense (8.9 g/cm^3), it is ductile and it is corrosion resistant. One manufacturer states that copper is ideal for high quality adhesive weights where small size, appearance and balance accuracy are important. One major UK manufacturer produces copper adhesive weights; copper wheel weights are not manufactured in Massachusetts.

Steel

Steel weights are susceptible to corrosion and therefore must be coated. One manufacturer uses a sacrificial zinc corrosion protection plus a plastic coating. Steel is not ductile and therefore it is more suited for adhesive weights than clip-on weights. Steel wheel weights are currently manufactured in Tennessee, Japan, UK, and Austria. Steel is a relatively inexpensive metal and it is possible that steel weights would cost less than lead weights. Steel is currently used for a wide range of products including automobile wheels and other automotive components.

Tin

One wheel weight manufacturer states that tin offers a high quality appearance with a good color match to alloy wheels and does not require corrosion protection. Tin wheel weights are currently manufactured by companies in India and the UK. No tin wheel weight manufacturers are located in Massachusetts. Based on the higher cost of tin, it is expected that tin wheel weights would cost more than lead weights.

Zinc and zinc alloy (ZAMAC – $ZnAl_4Cu_1$)

Zinc has a density of 7.05 g/cm^3 which is 62% of the density of lead and therefore zinc wheel weights will have the disadvantage of being larger than lead weights. Zinc is successfully being used for both clip-on and adhesive type wheel weights.

Zinc and/or zinc alloy wheel weights are manufactured by companies in Tennessee, Austria, Germany, Thailand, and the UK. No zinc wheel weight manufacturers are located in Massachusetts. Zinc clip-on weights are typically more expensive than uncoated lead clip-on weights but zinc weights are likely to be comparable in price to higher quality coated lead weights. Unless zinc weights are clearly marked or labeled, they are not easily distinguishable from lead weights and therefore will likely cause contamination problems for lead smelters during the recycling of lead wheel weights.

Based on the previously listed criteria, alternatives based on the following materials were given a lower priority for assessment

1. Tungsten: Tungsten has the advantage of being more dense than lead and could be used as a pure metal, as an alloy with other metals, or as a filler for plastic weights. A study by Okopol Institute for Ecology and Political Affairs concluded that tungsten was not a realistic alternative for lead wheel weights due to the high price of tungsten, which could be 100 times the price of lead. The study also stated that world-wide production of tungsten is only 31,500 tons per year while demand for wheel weights is 12,000 tons per year.
2. Iron: Iron was not found to be used for wheel weights, most likely because iron is not corrosion resistant.
3. Plastic (Polypropylene): A European study on the use of heavy metals in vehicles (Lohse, 2001) identified talc filled polypropylene as an alternative material for wheel weights but additional information on the use of polypropylene was not located. Polypropylene has the disadvantages of being a low density materiel and having a low melting point. The European study indicated

that talc filled wheel weights have a density of less than 5.2 g/cm^3, which is less than half the density of lead, and that they would fail at temperatures above 120° C.

4. Internal Balancing Systems: Internal balancing systems incorporate the weights, such as plastic beads, inside the tire. One advantage of internal balancing systems is that the weights will not fall off of the wheel since they are contained within the tire. These systems are also likely to be dynamic balancing systems, providing balancing even as the tire wears. A major barrier to adopting internal balancing systems is that they are not drop-in replacements to lead wheel weights. They are likely to require changes to tire balancing equipment and/or tire designs.

High Priority Alternatives for Lead Wheel Weights

The following alternative materials were selected for assessment:

- Copper
- Steel
- Tin
- Zinc and Zinc Alloy (ZAMAC)

3.3.3 Alternatives Associated with Fishing Sinkers

Available Alternatives

The following were identified as potential alternatives to lead fishing sinkers:

- Bismuth and bismuth/tin
- Brass
- Tin
- Copper
- Iron
- Ceramic
- Zinc
- Steel
- Tungsten, tungsten/nickel alloy and tungsten/polymer composite

Alternatives Prioritization

Alternatives that appeared likely to meet the following performance criteria were given a higher priority for assessment

- Adequate density to minimize size
- Smooth finish to reduce line wear
- Corrosion resistance
- Durability
- Scent absorption (some applications)
- Coloring (some applications)

Bismuth

Bismuth has successfully been used as a replacement for lead for some fishing sinker applications. One manufacturer of bismuth fishing sinkers is located in Minnesota.

Bismuth worm weights were found to be 3 to 6 times the cost of the equivalent lead weights. Preliminary research indicates that bismuth is a less toxic alternative to lead for use in fishing sinkers. The EPA stated that it did not discover any information on the toxicity of bismuth to avian or aquatic species (USEPA 1994).

Ceramic

Ceramic has successfully been used as a replacement for lead for some fishing sinker applications. Ceramic is less dense than lead and therefore ceramic weights are larger than lead weights. The larger size of ceramic weights could be a disadvantage in some applications but one manufacturer states that the larger size and lower density of ceramic weights decreases snags and the likelihood of getting caught on rocks. The color and noise created when using ceramic sinkers is also said to attract fish. Ceramic weights are currently produced by at least one manufacturer in Pennsylvania, but ceramic sinkers are not available at some of the major online fishing equipment retailers. Ceramic sinkers are likely to cost more than equivalent lead sinkers.

Steel

Steel has successfully been used as a replacement for lead for some fishing sinker applications. Steel is less dense than lead and therefore steel weights are larger than lead weights. In order to prevent corrosion, the steel weights must be coated or be made from a stainless steel. Steel fishing sinkers are produced by several companies in the U.S. and Canada. Steel sinkers can be cost competitive with lead sinkers. For some sizes, the price of steel egg sinkers was only 75% of the price of equivalent lead sinkers.

The EPA stated that it did not discover any information on the toxicity of steel to mammalian or aquatic species. EPA believes that steel would have low potential toxicity to those species. No adverse toxicological effects from steel have been indicated as a result of a research program conducted by the Fish and Wildlife Service to replace lead shot with steel shot, which examined toxicity to ducks of five proposed substitute shot metals (USEPA 1994).

Tin

Tin is widely used as a substitute for lead split-shot fishing weights because its ductility meets the requirements of this application. At 7.35 g/cm^3, tin is not as dense as lead and therefore the tin weights would be larger but it is not clear that this is either an advantage or disadvantage. Tin fishing sinkers are produced by several companies in the U.S. and Canada. At one major fishing equipment retailer, tin reusable split-shot sinkers are 1.5 to 2.5 times the price of the equivalent lead sinkers, depending on size and quantity.

EPA states that tin, in the inorganic form, is generally much less toxic to aquatic organisms than lead because of its low solubility, poor absorption, low uptake rate, and rapid excretion. It appears that tin is much less toxic to waterbirds and mammals than lead. (United States Environmental Protection Agency (USEPA 1994).

Tungsten

Tungsten has successfully been used as a replacement for lead for some fishing sinker applications. Manufacturers state that tungsten fishing sinkers have the advantage of being smaller and harder than lead sinkers and therefore are less likely to get hung-up on rocks. They also claim that fish are attracted to the noise created by tungsten sinkers.

Tungsten fishing sinkers are manufactured by several companies in the U.S. and Canada, including at least one company in Massachusetts. Tungsten worm weights were found to be 7 to 11 times the cost of the equivalent lead weights.

The EPA stated that it did not discover any information on the toxicity of tungsten to avian species. Tungsten was found to have low toxicity to aquatic organisms (crustaceans and algae). The toxicity of tungsten to aquatic organisms (daphnids and algae), and mammals (rats) is less than lead based on laboratory studies (USEPA 1994).

Based on the previously listed criteria, alternatives based on the following materials were given a lower priority for assessment

1. Brass: Brass is an alloy of zinc, copper, and lead. The lead in brass may be either intentionally added or exist as an impurity. EPA stated that even though the toxicity of brass to waterbirds has not been tested, based on the toxicity of lead and zinc, brass with and without lead would also be very toxic to waterbirds.
2. Copper: EPA states that laboratory studies indicate that copper is more toxic to aquatic organisms and algae than lead. However, EPA believes that environmental conditions in freshwaters would mitigate the toxicity of copper metal to aquatic organisms. The toxicity of copper to avian species is less than that of lead.
3. Iron: Iron was not found to be used for fishing sinkers, most likely because iron is not corrosion resistant.
4. Zinc: EPA found that zinc is more toxic to aquatic organisms than lead, that it may be bioconcentrated by invertebrates and algae, and it may be more bioavailable to aquatic organisms. EPA believes that environmental conditions could mitigate the toxicity of zinc to a certain extent in freshwaters to aquatic organisms because it is more soluble than lead. Zinc is toxic to mammals and avian species (USEPA 1994).

High Priority Alternatives

The following alternative materials were selected for assessment for fishing sinkers:

- Bismuth
- Ceramic
- Steel
- Tin
- Tungsten

3.3.4 Alternatives Associated with Heat Stabilizers for PVC Wire & Cable Coatings

Available Alternatives

The following were identified as potential alternatives to lead-based heat stabilizers for PVC in wire and cable:

- Mixed metal stabilizers based on:

  - Calcium-zinc
  - Barium-zinc
  - Magnesium-zinc
  - Magnesium aluminum hydroxide carbonate hydrate
  - Magnesium zinc aluminum hydroxide carbonate
  - Barium-calcium-zinc
  - Barium-cadmium-zinc
- Ester thiol
- Organotins

Alternatives Screening

The only alternative that was screened out was the barium-cadmium-zinc alternative based on the carcinogenicity criterion. The U.S. EPA has classified cadmium as a Group B1 carcinogen, a probable human carcinogen. IARC has classified cadmium as a Group 2A, probable human carcinogen.

Alternatives Prioritization

Stakeholders provided input on performance criteria, including:

- Heat stabilizer requirements for PVC processing at temperatures between 160 to 210 degrees Celsius. Also, the stabilizers elevate the resistance of PVC products during use against moisture, visible light, ultraviolet rays, and heat.
- Basic properties of lead that make it desirable for use as a heat stabilizer in PVC wire and cable applications
- Alternatives identified to date, including various mixed metal and organotin technologies.

There were many alternatives to lead available for use as a heat stabilizer for PVC wire and cable applications. Since there are so many alternatives for this use of lead, the Institute was not able to fully evaluate them all in the short time span allowed for this project. Therefore, we conducted an evaluation to determine those alternatives that are most feasible, and/or those alternatives that were representative of a class of alternatives, based upon the criteria listed earlier in this section. Based upon applying the criteria, the following five alternatives for using lead as a heat stabilizer were selected as high priorities for assessment:

1. Calcium-zinc
2. Barium-zinc
3. Magnesium-zinc
4. Magnesium aluminum hydroxide carbonate hydrate
5. Magnesium zinc aluminum hydroxide carbonate

All of the five alternatives can be categorized as mixed metal stabilizers. This family of stabilizers has achieved growing market acceptance as a non-lead heat stabilizer for PVC wire and cable applications. Each of the five alternatives is manufactured by at least one major heat stabilizer manufacturer.

Based on the previously listed criteria, alternatives based on the following materials were given a lower priority for assessment

The ester thiols and organotin alternatives were available for use as a heat stabilizer for flexible PVC applications. However, commercially available products were not found for specific use in PVC wire and cable applications.

High Priority Alternatives

The following alternative materials were selected for assessment for PVC heat stabilizers in wire and cable:

- Calcium-zinc
- Barium-zinc
- Magnesium-zinc
- Magnesium aluminum hydroxide carbonate hydrate
- Magnesium zinc aluminum hydroxide carbonate

3.4 Lead Alternatives Assessment

3.4.1 Alternatives Assessment for Ammunition for Shooting Ranges

Technical Assessment

The focus of this assessment is on alternatives to lead bullets used in handgun training ammunition for use at indoor firing ranges. Ammunition marketed for training applications is designed to be inexpensive and is not designed to meet the performance criteria required for service or duty ammunition. Ammunition designed for competitions, hunting or for use by law enforcement is typically more costly than training ammunition because it is designed for increased accuracy or has features, such as a hollow point, which improve performance for the intended application.

It should be noted that conventional handgun ammunition contains lead in both the projectile (bullet) and the primer. However, the scope of this assessment is limited to alternatives to the lead used for the projectile.

Lead-free or reduced lead ammunition is available in the following configurations:
Totally Lead-Free: Lead-free bullets and lead-free primer.
Lead-Free Primer: Lead bullets with lead-free primer. Ammunition with lead-free primer and a lead bullet with a copper jacket that has a totally enclosed base is referred to as firing line safe ammunition because these features reduce the lead vapor generated during firing.
Lead-free Bullets: Lead-free bullets with conventional primer, which contains lead and other heavy metals.
Frangible Lead-Free Bullets: Lead-free bullets that break up into small fragments upon impact with a hard target. Frangible ammunition may utilize either conventional or lead-free primer.

Longevity/Life in Service

The shelf-life of conventional handgun ammunition can be virtually indefinite if it is stored in a cool, dry environment, free of contaminants (Patterson 2006b). It is the primer that typically limits the shelf-life because it is most susceptible to degradation from elements such as excess heat, moisture, and contaminants. The bullet material does not affect the shelf-life of ammunition and several ammunition manufacturers state that their ammunition with lead-free bullets and conventional lead primer has the same shelf-life as conventional lead ammunition.

Key Standards for Component/End-product

U.S. standards for firearms and ammunition are developed and promulgated by the Sporting Arms and Ammunitions Manufacturers' Institute, Inc. (SAAMI), an accredited standards developer for ANSI. SAAMI was established to standardize case and chamber specifications so any ammunition of a given caliber and type will fit and function safely in any firearm designed for that caliber and type of ammunition. SAAMI standards define the safe range of internal ballistic pressures for a given firearm/ammunition combination and provide specifications required to achieve the safe pressures. (Sporting Arms and Ammunitions Manufacturers Institute, Inc. (SAAMI) 2006) Gun manufacturers recommend the use of ammunition with internal ballistic pressures that meet SAAMI specifications.

The Bureau of Alcohol, Tobacco and Firearms (BATF) has banned handgun ammunition made from the following materials because it may be considered armor piercing: tungsten alloys, steel, iron, brass, bronze, beryllium copper and depleted uranium. These materials can be used if the projectiles are frangible and are intended for target shooting applications. The ammunition considered in this study used frangible projectiles (bullets) with the exception of the solid copper bullets and the jacketed stranded zinc bullets and this ammunition was intended for target shooting. Therefore, none of the alternatives were classified by BATF as armor piercing (Bureau of Alcohol, Tobacco, Firearms and Explosives (BATF)).

Key Physical Characteristics and Key Performance Requirements

Density:

The relatively high density of lead (11.34 g/cm^3) is one of the properties that make it the primary material used for bullets. With a density of 19.3 g/cm^3, tungsten has the highest density of the alternatives in this assessment, followed by bismuth (9.8 g/cm^3), copper (8.9 g/cm^3), iron (7.8 g/cm^3), and zinc (7.10 g/cm^3) (Automation Creations).

Hardness and Malleability:

Lead is a soft malleable metal. These characteristics help to limit internal pressures generated when a firearm is fired. It is critical that internal pressures are limited to avoid damage to the firearm and potentially dangerous conditions. The malleability of the bullet is one of several factors that affect internal pressures. When the propellant is ignited and first starts to push the bullet into the rifling, internal pressures rise dramatically. The softness and malleability of lead and the traditional construction of jacketed lead bullets provide cushioning and serve to reduce the initial peak pressure.

The base metals used for the lead-free alternatives are harder than lead as can be seen in Table 3.4.1A. However, information on the actual hardness and malleability of the alternatives was not available because the alternatives are composed of alloys or mixtures of metal powder and other materials such as plastic. If the softness and malleability of the alternatives is not sufficient to limit internal pressures, the manufacturer can limit peak pressures by making other design changes such as reduced power loading, changing the propellant formulation, using softer jacket material or making dimensional changes.

Table 3.4.1 A: Hardness of Ammunition Base Metals

Material	Hardness		
	Brinell Scale	Mohr's Scale	Vickers Scale
Lead	4.2	1.5	5
Zinc		2.5	30
Copper		3	50
Steel (carbon)	170	5-6	
Tungsten	294	7	

Bullet weight:

The mass of a bullet affects the ballistic performance of ammunition and, for many applications, a higher bullet mass is desirable. The mass of a bullet is a function of the size of the bullet and the density of the bullet material. However, the size of the bullet is dictated by gun dimensions and therefore the bullet weight is driven primarily by the density of the bullet material.

Lead bullets are often available in two or three weights for a given caliber while lead-free bullets are generally available in only one weight for a given caliber. A lead-free bullet typically has a mass that is equal to, or less than, the smallest lead bullet available in that caliber. For example, lead 9 mm ammunition is available in 115, 124 and 147 grain (15.43 grains = 1 gram) bullet weights while 9 mm ammunition with lead-free bullets typically has a bullet weight of 115 grains or less.

According to a manufacturer of bismuth ammunition, Bismuth Cartridge Co., since bismuth is nearly as dense as lead it is possible to manufacture bismuth frangible bullets that match the weight of many lead bullets. For example, the company produces 9 mm frangible bismuth ammunition in 115 grain and 124 grain bullet weights.

The lower density of copper results in bullets that have less mass than equivalent lead bullets. For example, frangible 9 mm ammunition composed of 90% powdered copper and 10% powdered tin is available from several manufacturers (Federal, International and Winchester) with bullet weights ranging from 90 to 100 grains. Ammunition composed of copper powder and a polymer was produced by PMC in the 9 mm caliber with a bullet weight of 77 grains. Solid copper 9 mm bullets are available from one manufacturer in a 115 grain bullet weight (Barnes Bullets).

Frangible 9 mm ammunition composed of powdered iron is available from at least one manufacturer with a 105 grain bullet weight (Remington Arms Company, Inc.). One ammunition manufacturer produced tungsten/nylon frangible 9 mm ammunition with a 115 grain bullet weight, but this product was discontinued (Nowak 2006). Stranded zinc 9 mm ammunition is available from at least one manufacturer with a 100 grain bullet weight (Federal Cartridge Company).

Recoil:

When training with a handgun, it is desirable to use training ammunition that provides the same "feel" as duty ammunition. One factor that affects the "feel" of firing a handgun is the amount of recoil and one of the factors that affect recoil is the weight of the bullet. Recoil is of particular concern for lead-free training ammunition, since lead-free bullets often have a lower bullet weight than lead duty ammunition.

Bismuth Cartridge Co. states that it can produce frangible bismuth ammunition for training that matches the recoil of duty load (lead ammunition) used by law enforcement agencies. (Bismuth Cartridge Company)In its law enforcement ammunition catalog, Federal Cartridge Co. states that the felt recoil of its BallistiClean stranded zinc core ammunition is comparable to service ammunition (Federal Cartridge Company).

A study conducted by the New Jersey Division of Criminal Justice found that several types of lead-free ammunition provided sufficient recoil to meet the "equivalent load" standard. In the 9 mm caliber, the following ammunition received a passing grade for felt recoil (Zamrok 2004):

- Bismuth Cartridge Co. No-Tox, 115 grain (bismuth with copper jacket)
- Federal CQT, 100 grain (stranded zinc with copper jacket)
- International Greenline, 75+P and 100 grain (powdered copper/tin)
- Speer Lawman RHT, 100 grain (copper)
- Winchester SF LE, 100+P grain (powdered copper/tin)
- Winchester SuperClean NT, 105 grain (tin core with copper jacket)

The following ammunition received a failing grade for felt recoil:

- Remington Disintegrator, 105 grain (iron powder with copper jacket)
- Delta 115 grain (copper)
- Winchester Ranger, 85 grain (tungsten/nylon)

Ammunition manufacturers usually provide information about the ballistics of their ammunition products, including bullet velocity, energy and trajectory. Bullet velocity and energy are typically measured at the muzzle of the gun (muzzle velocity and muzzle energy) as well as at certain distances, such as 50 and 100 yards. The values for bullet velocity and energy used in this assessment were those measured at the muzzle of the gun because these values were the most readily available. Data were gathered on the muzzle velocity and muzzle energy of 9 mm lead and lead-free handgun bullets.

There are a number of factors that affect bullet velocity and energy, including bullet weight and the amount of gunpowder in the cartridge. With all other factors equal, a lead-free bullet must have the same weight as a lead bullet to achieve the same bullet velocity and energy. Bullet velocity affects bullet energy and some manufacturers increase velocity for the lighter lead-free bullets to reach the target bullet energy. Due to the number of factors that affect bullet velocity and energy, this assessment did not attempt to compare the performance of lead-free bullets with lead bullets in this area.

Table 3.1.4 B lists examples of the bullet muzzle velocity and muzzle energy for both lead and lead-free ammunition.

Table 3.4.1 B: Muzzle Velocity and Muzzle Energy Comparison

Bullet Material	Manufacturer	Bullet Description Caliber Weight	Muzzle Velocity (ft/s)	Muzzle Energy (ft-lb)
Bismuth	Bismuth Cartridge	Frangible, copper jacket 9 mm 115 grain	1150	338
Copper/tin	International Cartridge	Frangible 9 mm 100 grain	1250	375
Iron	Remington	Frangible 9 mm 115 grain	1220	350
Lead	Remington	Copper jacket 9 mm 115 grain	1135	329
	Federal Cartridge	Copper jacket 9 mm 115 grain	1160	345
	Winchester	Copper jacket 9 mm 115 grain	1190	362
Tungsten/ nylon	Winchester (discontinued product)	Frangible 9 mm 85 grain	1450	335
Zinc	Federal Cartridge	Stranded zinc core with copper jacket 9 mm 100 grain	1230	335

Source: Information compiled from manufacturer websites and performance data sheets.

Terminal Ballistics

Many of the lead-free bullets reviewed in this assessment are frangible, which means they fragment into small particles upon impact with a target. Frangible lead-free bullets are typically viewed as being safer than lead bullets for use at indoor firing ranges because they reduce or eliminate the dangers associated with ricocheting bullet fragments. This is of particular concern when firing at steel targets at close range. Frangible bullets can also limit damage to steel targets. Frangible lead bullets are not currently available.

Frangible bullets made of bismuth, iron, tungsten/nylon or powdered copper fragment into dust when shot into steel targets, reducing the potential for ricochet. The Remington frangible iron ammunition is reduced to dust with fragments of copper from the plated jacket. Remington test data show that 64.5% of the particles hit the floor within 5 ft and 97.2% within 10 ft.

The core of the stranded zinc ammunition consists of zinc cables arranged in a spiral fashion. The cables break apart upon entering a target (Federal Cartridge Company). It is not clear whether stranded zinc ammunition ricochets more or less than lead bullets.

Solid copper bullets are not frangible and may ricochet more than lead bullets because copper is stiffer than lead (Jones 2001).

Barrel Fouling and Barrel Wear

When a bullet is fired, the ignition of the gunpowder generates both heat and pressure. The pressure forces the bullet down the barrel of the gun, where the rifling is engraved into the bullet. This rifling in the barrel causes the bullet to spin. Depending on the bullet composition and design, the combination of pressure, friction and heat can cause the bullet material to smear on the bore of the barrel. If the bullet material smears, it will leave a build-up of bullet material on the barrel. This residual bullet material, combined with residue from the primer and gunpowder, causes barrel fouling. Barrels must be cleaned and cared for to limit barrel fouling, since this build-up of residue can affect accuracy and performance and excessive build-up of material on the bore can increase pressure to a dangerous level. There are a number of factors that affect the amount of barrel fouling, including the bullet material or, if the bullet is jacketed, the jacket material. Guilding metal, which has copper as a main ingredient, is commonly used to jacket conventional lead bullets. Lead-free bullets may use a softer copper jacket to help reduce peak pressures if the alternative material lacks malleability (Patterson 2006b).

Barrel wear is the erosion of barrel material by the bullets and the heat and pressure generated by the burning propellant (Patterson 2006b). There are a number of factors that affect barrel wear including the hardness of the bullet or bullet jacket, malleability of the bullet material, the construction of the bullet, and the hardness of the gun barrel.

Bismuth Cartridge Co. states that use of its bismuth ammunition will not cause more barrel-fouling than conventional lead ammunition and that use of its bismuth ammunition will not cause more barrel wear than conventional lead ammunition (Flaherty 2006).

According to one manufacturer, the copper used for solid copper bullets is softer than the copper alloy commonly used for jacketing of lead bullets. This manufacturer (Barnes) reduces barrel fouling by heat treating the bullets and by adding grooves to the bullet shank, which reduces fouling by providing a relief area for displaced copper. Barnes states that any copper barrel fouling can be cleaned using ammonia-based cleaners (Barnes Bullets).

Remington states that the copper plating on its Disintegrator iron core bullets provides a smooth, ductile jacket that enhances feed and function in all auto-loading pistols, minimizes barrel fouling, and virtually eliminates barrel erosion (Remington Arms Company, Inc.).

In its law enforcement ammunition catalog, Federal Cartridge Co. states that the heavy metal-free primer and lead-free bullets of its BallistiClean stranded zinc core ammunition help to reduce barrel fouling. The stranded zinc ammunition is plated with a copper jacket and therefore barrel wear is expected to be similar to other copper jacketed ammunition (International Cartridge Corp).

Financial Assessment

Initial Purchase Price for Chemical/Alternative

Lead is significantly less expensive than any of the alternatives in this assessment, with the exception of iron. The Platts Metals Week North American producer price for lead was $0.65 per pound in December 2005. The dealer prices for bismuth fluctuated from an average of $3.55 per pound in the first quarter of 2005 to an average of $4.57 per pound in the fourth quarter of 2005. The 2005 fourth quarter price represented a 33% increase over the 2004 fourth quarter price. The December 2005 price for copper (U.S. producer cathode) was $2.23 per pound. Iron is not traded on an exchange (e.g. London Metals Market) but the price for hot rolled steel plate, which was $0.29 per pound in December 2005, suggests that the price of iron is competitive with lead. (Metals

Consulting International (MCI))Tungsten prices fluctuated from approximately $2.72 per pound in January 2005 to approximately $9.98 per pound in May 2005. (DesLauriers 2005) The Platts Metals Week (North American Special High Grade) price for zinc was $0.88 per pound in December 2005.

Initial Purchase Cost for End-product/Component

Ammunition with lead-free bullets or lead-free frangible bullets is marketed primarily to law enforcement agencies and the military and therefore consumer prices for lead-free handgun ammunition were not readily available.

A study conducted by the New Jersey Division of Criminal Justice found the following regarding the purchase price for reduced lead and lead-free ammunition(Zamrok 2004):

- Lead training ammunition was approximately half the cost of lead service ammunition
- Firing line safe training ammunition with lead-free primer and totally encapsulated lead core projectiles cost an additional $2 to $20 per 1000 rounds over lead training ammunition, depending on caliber and manufacturer
- Lead-free training ammunition (lead-free primer and projectile) cost $30 to $40 more than lead service ammunition per 1,000 rounds
- Frangible lead-free training ammunition cost $100 more than lead service ammunition per 1,000 rounds (9mm caliber)

A search of online ammunition retailers found that the cost of lead training ammunition for indoor shooting ranges (9mm, 115 grain, full metal jacket) varied from $0.14 to $0.20 per round. The cost of lead-free training ammunition (copper, copper/tin, iron, and tin/copper) was at least double that of lead training ammunition. The prices found for lead-free 9mm training ammunition ranged from $0.30 to $0.70 per round. In comparison, firing line safe training ammunition with lead-free primer and totally encapsulated lead core projectiles could be purchased for a 10-20% premium over lead training ammunition.

Winchester produces frangible handgun training ammunition (Ranger SF) that is composed of 90% powdered copper and 10% powdered tin with a non-toxic primer. The price of this product (9 mm caliber) is approximately 2.3 times the price of conventional lead training ammunition. Winchester also produces lead-free training ammunition (Super Clean NT) that is composed of a solid tin core with a copper jacket. This ammunition is not frangible. The price of this product for a 9 mm handgun is about two times the price of conventional lead training ammunition (Nowak 2006).

Pricing for bismuth and tungsten ammunition was not available because they are sold only to law enforcement agencies.

Availability of Chemical/Alternative

Bismuth, and tungsten are relatively scarce metals with a limited reserve base, while copper, iron (steel) and zinc are more abundant than lead (European Commission Enterprise Directorate-General 2004).

All primary bismuth consumed in the U.S. is imported and less than 5% is obtained by recycling old scrap. Most bismuth is produced from mines in Mexico, China, Peru and Bolivia. It is a byproduct of processing lead ores, and in China, it is a byproduct of tungsten ore processing. Reported bismuth consumption was 2,120 metric tons in 2003 in the U.S. Worldwide demand is growing at about 5% per year, driven in part by its use as a replacement for lead but a global shortage is not expected. However, the supply could be constrained by low prices (Carlin, James F. Jr.).

In 2005, the worldwide mine production of copper was 16.4 million tons but strong growth in China and India resulted in a global production deficit. In 2006, increased capacity is expected to result in a modest production surplus (Edelstein 2006).

In 2004, worldwide trade in iron ore was approximately 670 million metric tons (Iron and Steel Statistics Bureau (ISSB)).

U.S. consumption of tungsten in 2005 was 11,600 metric tons. World tungsten supply is dominated by Chinese production and exports. The Chinese government regulates tungsten production and the total volume of tungsten exports, and the government has gradually shifted the balance of export quotas towards value-added downstream tungsten materials and products. In 2005, inadequate supplies of tungsten concentrates within China combined with increased demand for tungsten materials in China and elsewhere resulted in steep increases in the prices of tungsten concentrates. In response to this price increase, the sole Canadian tungsten mine restarted operations and action was taken to develop tungsten deposits or reopen inactive tungsten mines in Australia, China, Peru, Russia, the United States, and Vietnam (Shedd 2006).

Worldwide, there was a 200,000 ton production deficit of zinc in 2005. In 2005, U.S. mine production of zinc was 837,800 tons, which accounted for less than one-third of the quantity consumed domestically. Canada and Mexico are leading sources of imported zinc (Gabby 2006).

Availability of Component/End-product

Lead-free handgun ammunition is produced by each of the leading ammunition manufacturers and a few smaller ammunition manufacturers specialize in the production of lead-free ammunition. Currently, the primary market for lead-free handgun ammunition is for law enforcement and military training applications. A few manufacturers also produce lead-free duty rounds. Lead-free ammunition is available in both solid bullet and frangible bullet designs. The bullets made with hard metals (iron and tungsten) must be frangible or they would be classified as armor-piercing bullets.

Handgun ammunition with frangible bismuth bullets is available from at least one manufacturer, Bismuth Cartridge Co. This manufacturer currently only markets its Bismuth Reduced Hazard Ammunition to law enforcement agencies. It is available with conventional, lead-free, or heavy metal free primers. The company manufactures round nose training ammunition and is in the final stages of research and development of a hollow-point duty bullet (Flaherty 2006).

The Bismuth Cartridge Co. website lists the following frangible bismuth ammunition products: 9 mm 115 grain round nose; .40 S&W 135 grain flat point; and .45 Auto 185 grain flat point. A company spokesperson said that it can provide custom bismuth training ammunition that duplicates the trajectories and recoil of an agency's duty load (Flaherty 2006). It also produces bismuth frangible duty rounds for applications where ricochet poses a hazard.

Several ammunition manufacturers produce handgun ammunition using bullets composed of a mixture of powdered copper and powdered tin, which is sintered to produce a frangible bullet. Copper is used by at least one manufacturer to produce solid copper bullets. Solid copper bullets are not frangible and are used for duty rounds, personal defense or hunting applications. Copper is also used as a jacketing material for many types of ammunition, including handgun ammunition with lead, bismuth, iron, and tin cores.

At least one ammunition manufacturer produces lead-free frangible handgun ammunition produced with iron powder. The projectile in Remington's Disintegrator Lead-Free Frangible ammunition is composed of powdered iron with an electroplated copper jacket. Remington markets its

Disintegrator product line to law enforcement agencies. Disintegrator ammunition is available in 9 mm, .40 S&W, and .45 ACP calibers.

Tungsten has been used recently for lead-free handgun ammunition but it could not be confirmed that it is currently produced by ammunition manufacturers. Winchester had produced handgun training ammunition with a tungsten/nylon bullet (Ranger DF) but this product was replaced by ammunition that uses a 90% copper/10% tin bullet (Ranger SF), which Winchester says is a better product. (Nowak 2006)Tungsten/nylon ammunition was used at the Massachusetts Military Reservation firing range at Camp Edwards from 1999 until February 2006, when its use was halted over concerns that tungsten was migrating into Cape Cod's groundwater (Lehmert 2006).

Zinc is used by Federal Cartridge Co. in its BallistiClean handgun ammunition, which is marketed to law enforcement for training. The bullet used in BallistiClean ammunition has a stranded zinc core and a copper jacket (Federal Cartridge Company).

Table 3.4.1 C lists the ammunition manufacturers known to produce handgun training ammunition with lead-free bullets:

Table 3.4.1 C: Ammunition Manufacturers

Manufacturer	Website	Description
Bismuth Cartridge Co.	www.bismuth-notox.com	Frangible bismuth core with copper jacket
CCI/Speer	http://le.atk.com	Frangible copper powder bullet
Federal Cartridge Co.	www.federalcartridge.com	Frangible copper/tin bullet
		Stranded zinc core with copper jacket
International Cartridge Co.	www.internationalcartridge.com	Frangible copper/tin bullet
Remington Arms and Ammunition	www.remingtonle.com	Frangible iron powder bullet with copper jacket
Winchester Ammunition	www.winchester.com	Frangible copper/tin bullet
		Tin core with copper jacket

Capital Costs

The lead bullet production process is significantly different from the production process used to produce frangible lead-free bullets. Production of lead bullets involves extruding a lead billet into wire, cutting the wire into slugs, and then pressing the slugs into the shape of a bullet. For jacketed bullets, a copper jacket is applied (National Research Council (NRC) 2004).

Frangible bullets made from powdered copper/tin or iron require a significantly different production process due to the fact that they are made from powdered metals. Bismuth frangible bullets are cast, swaged and then plated with a copper jacket (Bismuth Cartridge Company).

Due to the differences in production processes, it is likely that switching a lead bullet manufacturing process to a lead-free manufacturing process would require significant capital investment. It should be noted however, that most of the major ammunition manufacturers already market ammunition with lead-free bullets, which means that they have either already invested in lead-free bullet production or they purchase lead-free bullets from a supplier. An expansion of the market beyond current production capacity would likely require significant additional capital expense.

Key Operating Costs During Use of End-product

Use of lead ammunition increases a firing range's operating costs since air monitoring and blood level testing of range officers must be conducted according to OSHA and EPA standards. Use of lead ammunition may also increase costs associated with maintenance of containment and filtration systems, purchase of replacement filters, range cleaning and hazardous waste disposal. By switching to lead-free ammunition, firing ranges can reduce or eliminate costs in these areas (Jones 2001; Massachusetts Division of Occupational Safety 2004).

Frangible bullets, including those made from bismuth, copper, iron and tungsten, fragment into dust when shot at mild steel targets, which reduces wear and damage to the targets, bullet traps and backstops at firing ranges.

Key End-of-Product Life Costs

Lead bullets and bullet fragments collected at indoor firing ranges are typically sold to lead recyclers and therefore may represent a source of revenue for firing ranges. At ranges where both lead and lead-free ammunition is used, certain types of lead-free bullets, such as zinc bullets, may contaminate the lead, making it unsuitable for recycling. (Vargas, 2004) Lead bullets may also be contaminated with other materials, such as materials used for bullet traps, which can decrease the recycling value or eliminate the possibility of recycling. Lead smelters separate the copper jacketing material from the lead and recycle it. Any lead that is not recycled must be disposed of as hazardous waste.

Bismuth, copper, iron, tungsten, and zinc bullets and bullet fragments collected at indoor firing ranges can be disposed of as non-hazardous material. These lead-free materials can also be collected for recycling. Information about the value of reclaimed bullets or bullet fragments made of these lead-free materials was not available but it should be noted that, with the exception of iron, the raw material prices for these alternatives are significantly higher than lead, which indicates the potential of higher values for the reclaimed materials.

A Department of Defense study estimated that the clean-up cost for a closed outdoor lead ammunition firing range can be up to $2.5 million, while the average cost to clean-up an indoor lead ammunition firing range is about $150,000 (Anonymous 2001).

The following tables provide additional financial data for lead ammunition alternatives.

Table 3.4.1 D: Ammunition for Shooting Ranges – Bismuth

	Financial Parameter	Measure/Metric	Source of Information
		Required Data	
	Initial purchase price for chemical/alternative	In 2005, bismuth dealer prices fluctuated from an average of $3.55 per pound in the first quarter to an average of $4.57 per pound in the fourth quarter. The fourth quarter 2005 price represented a 33% increase over the fourth quarter 2004 price. Lead raw material price: $0.65 per pound, Platts Metals Week North American producer price, December 2005	Carlin, 2006a Gabby, 2006a
	Initial purchase cost for end-product/component	Pricing for bismuth ammunition was not available because it is sold only to law enforcement agencies.	

Table 3.4.1 D: Ammunition for Shooting Ranges – Bismuth

	Financial Parameter	Measure/Metric	Source of Information
	Availability of chemical/alternative	Bismuth consumption in the U.S. in 2005 was estimated at 2,280 metric tons. Worldwide demand is growing at about 5% per year, driven in part by its use as a replacement for lead but a global shortage is not expected. Low prices could constrain bismuth supply to the market.	Carlin, 2006a
	Availability of component/end-product	Bismuth frangible ammunition is available from at least one manufacturer, Bismuth Cartridge Co. This manufacturer currently only markets its Bismuth Reduced Hazard Ammunition to law enforcement agencies.	Flaherty, 2006 Bismuth, 2006
	Key end-of-product life costs	The bismuth core fragments into dust when shot into mild steel targets. The bullet particles can be swept up and disposed of as non-hazardous material.	
	Capital costs	Bismuth frangible bullets are cast, swaged and then plated with a copper jacket. (Bismuth, 2006) This manufacturing process differs from the lead bullet manufacturing process, and therefore, it is likely that switching to bismuth bullet manufacturing would require significant capital investment.	Bismuth, 2006

Table 3.4.1 E: Ammunition for Shooting Ranges – Copper

	Financial Parameter	Measure/Metric	Source of Information
		Required Data	
	Initial purchase price for chemical/alternative	Copper raw material price: $2.23 per pound, U.S. producer cathode, December 2005 Lead raw material price: $0.65 per pound, Platts Metals Week North American producer price, December 2005	Edelstein, 2006 Gabby, 2006a
	Initial purchase cost for end-product/component	Winchester produces frangible handgun training ammunition (Ranger SF) that is composed of 90% powdered copper and 10% powdered tin with a non-toxic primer. The cost of this product for a 9 mm handgun is about 2.3 times more than conventional lead training ammunition. Winchester also produces lead-free training ammunition (Super Clean NT) that is composed of a solid tin core with a copper jacket. This ammunition is not frangible. The cost of this product for a 9 mm handgun is about two times more than conventional lead training ammunition.	Nowak, 2006
	Availability of chemical/alternative	In 2005, the worldwide mine production of copper was 16.4 million tons but strong growth in China and India resulted in a global production deficit. In 2006, increased capacity is expected to result in a modest production surplus. (USGS)	Edelstein, 2006

Table 3.4.1 E: Ammunition for Shooting Ranges – Copper

	Financial Parameter	Measure/Metric	Source of Information
	Availability of component/end-product	Several ammunition manufacturers produce frangible handgun ammunition using bullets produced by Sinterfire, which are composed of a mixture of powdered copper and powdered tin. Copper is also used as a jacketing material for many types of ammunition, including handgun ammunition with lead, bismuth, iron, and tin cores. At least one ammunition manufacturer produces handgun ammunition with a solid copper bullet. Solid copper bullets are not frangible and are used for duty rounds, personal defense or hunting applications.	
	Capital costs	Frangible bullets made from powdered copper require a significantly different production process due to the fact that they are made from powdered metals. Therefore, it is likely that switching a lead bullet manufacturing process to a powdered copper bullet manufacturing process would require significant capital investment.	
		Additional Data if Available	
	Key end-of-product life costs	Frangible copper bullets fragment into dust when shot into mild steel targets. The bullet particles can be swept up and disposed of as non-hazardous material.	

Table 3.4.1 F: Ammunition for Shooting Ranges – Iron

	Financial Parameter	Measure/Metric	Source of Information
		Required Data	
	Initial purchase price for chemical/alternative	Iron and iron powder are not traded on an exchange such as the London Metal Exchange and therefore pricing was not readily available.	
	Initial purchase cost for end-product/component	Remington's Disintegrator Lead-Free Frangible ammunition is available at several online ammunition retailers. Prices for 9mm, 100 grain ammunition ranged from $0.35 to $0.53 per round.	
	Availability of chemical/alternative	In 2004, worldwide trade in iron ore was approximately 670 million metric tons.	ISSB, 2006
	Availability of component/end-product	At least one ammunition manufacturer produces lead-free frangible handgun ammunition produced with iron powder. The projectile in Remington's Disintegrator Lead-Free Frangible ammunition is composed of powdered iron with an electroplated copper jacket. Remington markets its Disintegrator product line to law enforcement agencies. Disintegrator ammunition is available in 9 mm, .40 S&W, and .45 ACP calibers.	Remington, 2005

Table 3.4.1 F: Ammunition for Shooting Ranges – Iron

	Financial Parameter	Measure/Metric	Source of Information
	Capital costs	Frangible bullets made from powdered iron require a significantly different production process due to the fact that they are made from powdered metals. Therefore, it is likely that switching a lead bullet manufacturing process to an iron bullet manufacturing process would require significant capital investment.	
		Additional Data if Available	
	Key end-of-product life costs	Frangible iron bullets reduce wear and damage to bullet traps and backstops at firing ranges.	Remington, 2005

Table 3.4.1 G: Ammunition for Shooting Ranges – Tungsten

	Financial Parameter	Measure/Metric	Source of Information
		Required Data	
	Initial purchase price for chemical/alternative	In 2005, tungsten prices fluctuated from approximately $2.72 per pound in January to approximately $9.98 per pound in May. Lead raw material price: $0.65 per pound, Platts Metals Week North American producer price, December 2005	DesLauriers, 2005 Gabby, 2006a
	Initial purchase cost for end-product/component	A study conducted by the New Jersey Division of Criminal Justice stated that the cost for Winchester's Ranger Frangible ammunition, which had a projectile made of tungsten/copper/nylon, was $428 per 1000 rounds or $.43 per round. This is two to three times the price of Winchester's USA training ammunition with a lead projectile and full metal jacket when purchased from online ammunition retailers. Winchester discontinued this tungsten product four years ago.	Zamrok, 2004
	Availability of chemical/alternative	U.S. consumption of tungsten in 2005 was 11,600 metric tons. In 2005, inadequate supplies of tungsten concentrates within China combined with increased demand for tungsten materials in China and elsewhere resulted in steep increases in the prices of tungsten concentrates.	Gabby, 2006a
	Capital costs	The process used to manufacture tungsten bullets is different than the lead bullet manufacturing process and therefore a switch from lead to tungsten bullets would require significant capital investment.	

Table 3.4.1 H: Ammunition for Shooting Ranges – Zinc

	Financial Parameter	Measure/Metric	Source of Information
Required Data			
	Initial purchase price for chemical/alternative	Zinc raw material price: $0.88 per pound, Platts Metals Week North American Special High Grade, December 2005 Lead raw material price: $0.65 per pound, Platts Metals Week North American producer price, December 2005	Gabby, 2006b Gabby, 2006a
	Initial purchase cost for end-product/component	Not available.	
	Availability of chemical/alternative	U.S. mine production in 2005 was 837,800 tons. Domestic zinc metal production capacity accounts for less than one-third of quantity consumed domestically. Canada and Mexico are leading sources of zinc. In 2005, there was a 200,000 ton production deficit worldwide. (USGS)	Gabby, 2006b
	Availability of component/end-product	Federal produces ammunition with a bullet that has a stranded zinc core and a copper jacket.	Federal, 2006
	Capital costs	The process used to manufacture bullets with a stranded zinc core is different than the lead bullet manufacturing process and therefore a switch from lead to zinc bullets would require significant capital investment.	
Additional Data if Available			
	Key end-of-product life costs	When zinc ammunition is used at a firing range where lead ammunition is also used, the zinc contaminates the lead making it unsuitable for recycling. The recovered mix of zinc and lead bullets must be disposed of as hazardous waste.	Vargas, 2004

Environmental Health and Safety

Numerous studies indicate that lead exposure can occur at shooting ranges where lead ammunition is used, particularly for range masters and instructors. The primary source of lead exposure is from the airborne lead particles and lead fumes released from the bullet during firing. When lead ammunition is used where the lead core is exposed at the base of the bullet, approximately 80% of the airborne lead comes from the bullet and the remaining 20% comes from lead styphnate in the primer and lead dust generated when the bullet hits the target (Noll, Clark 1997; Simpson 1993; Fischbein 1980).

Results from evaluations of exposures to lead in indoor law enforcement firing ranges by NIOSH showed that shooters had a mean lead exposure of 110 $\mu g/m^3$ (8-hour, TWA) when firing lead bullets. Eighty nine percent exceeded the OSHA PEL for occupational exposure to lead (50 $\mu g/m^3$, 8-hour, TWA) (Centers for Disease Control (CDC) 1983).

The National Association of Shooting Ranges (NASR) lists fifty-five handgun shooting ranges in Massachusetts, most of them with indoor shooting ranges. The handgun ammunition used at these ranges is almost exclusively ammunition with bullets made of lead and primer that contains lead and other heavy metals. A spokesperson from the Sporting Arms and Ammunition Manufacturers Institute (SAAMI) said that, to his knowledge, Massachusetts does not have any lead-free indoor firing ranges with the possible exception of those used by law enforcement and the military (Patterson 2006a).

Environmental Assessment

Drinking Water Standards

The National Primary Drinking Water Regulations are legally enforceable standards, set by EPA, that apply to public water systems. In these standards, the Maximum Concentration Level (MCL) for lead in drinking water is 15 μg/L and the Maximum Concentration Level Goal (MCLG) is zero. Copper is the only alternative ammunition material in this assessment for which EPA has set an MCL. Copper has an MCL of 1300 μg/L.

EPA has also established National Secondary Drinking Water Standards, which are non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water. The following list shows the alternative ammunition materials included in these secondary standards:

- Copper: 1000 μg/L
- Iron: 300 μg/L
- Zinc: 5000 μg/L

Affinity for Water: Water Solubility

Lead, bismuth, copper, and iron are insoluble in water. Tungsten dissolves in water reaching concentrations up to 475 – 500 mg/L (Strigul, Nicolay et al. 2005). Zinc is soluble in water but the solubility is dependent on the properties of the water, such as acidity, temperature, chlorine concentration and hardness. It should be noted that certain compounds of these metals may be soluble.

Density

The density of lead is 11.34 g/cm^3. With a density of 19.3 g/cm^3, tungsten has the highest density of the alternatives in this assessment, followed by bismuth (9.8 g/cm^3), copper (8.9 g/cm^3), iron (7.8 g/cm^3), and zinc (7.10 g/cm^3) (Automation Creations).

Bioaccumulation

According to the International Chemical Safety Cards (ICSCs), bioaccumulation of lead may occur in plants and mammals and it is strongly advised that lead does not enter the environment. Specific information on the bioaccumulation of copper, tungsten, zinc, bismuth and iron were not available. As discussed in earlier in this report, EPA is in the process of developing a framework that will address the issue of bioaccumulation of metals, as well as related issues such as bioavailability.

Aquatic toxicity

National Recommended Water Quality Criteria was used as a source for data on aquatic toxicity of lead and lead-free alternatives. Water Quality Criteria includes the following two aquatic life criteria for both freshwater and saltwater:

- Criteria Maximum Concentration (CMC) – An estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.

- Criteria Continuous Concentration (CCC) – An estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

Lead, copper and zinc are listed as Priority Toxic Pollutants and iron is listed as a Non Priority Pollutant. Bismuth and tungsten were not included in the Water Quality Criteria list. The following table shows the Water Quality Criteria for lead, copper, iron and zinc.

Table 3.4.1 I: Water Quality Criteria Comparison

Priority Pollutant	Freshwater		Saltwater	
	CMC (μg/L)	**CCC (μg/L)**	**CMC (μg/L)**	**CCC (μg/L)**
Lead	65	2.5	210	8.1
Copper	13	9.0	4.8	3.1
Iron	-	1000	-	-
Zinc	120	120	90	81

The Water Quality Criteria values indicate that lead, copper and zinc are toxic to aquatic organisms, even at relatively low concentrations.

In 1994, EPA addressed the aquatic toxicity of alternatives to lead fishing sinkers in its response to citizens' petition and proposed ban for lead fishing sinkers. In its assessment of aquatic toxicity of lead alternatives, EPA made the following statements about copper and zinc: "Laboratory studies indicate that copper is more toxic to aquatic organisms, such as fish, crustaceans, worms, and algae than lead." (United States Environmental Protection Agency (USEPA) 1994). However, EPA believes that environmental conditions in freshwaters would mitigate the toxicity of copper to aquatic organisms. Zinc is more toxic to aquatic organisms (fish and crustaceans) than lead and it may be more bioavailable to aquatic organisms than lead. "Tungsten was found to have low toxicity to aquatic organisms (crustaceans and algae)" (United States Environmental Protection Agency (USEPA 1994). EPA stated that it did not find any information to indicate that bismuth or iron is toxic to aquatic species.

Human Health Assessment

Acute Human Effects: Occupational Exposure Limits

Lead exposure can occur at indoor shooting ranges from airborne lead particles and lead fumes released during firing. In general, the lead-free ammunition alternatives have less stringent occupational exposure limits than lead.

- *IDLH*

  The Immediately Dangerous to Life or Health Concentrations (IDLH) for lead is 100 mg/m^3. The IDLH for copper is also 100 mg/m^3. There are no data on IDLH for bismuth, tungsten and zinc. For iron, the IDLH is 2,500 mg Fe/m^3; 1-2 grams may cause death but 2-10 is usually ingested in fatal cases.

- *PEL*

The Permissible Exposure Level (PEL) for lead is 0.050 mg/m^3 (8-hour TWA). The PEL (TWA) for copper is 1 mg/m^3. The PEL for iron oxide is 10 mg Fe/m^3. PELs have not been established for bismuth, steel, tungsten and zinc; however, PELs have been set for zinc chloride (1 mg/m^3) and zinc oxide (5 mg/m^3).

- *REL*

The Recommended Exposure Level (REL) for lead is 0.050 mg/m^3 (TWA). The REL (TWA) for copper is 1 mg/m^3; for steel (iron) is 5 mg Fe/m^3; and for tungsten is 5 mg/m^3. An REL has not been established for bismuth or zinc.

- *TLV*

The ACGIH TLV for tungsten is 5 mg/m^3, for copper is 1 mg/m^3, for iron oxide is 5 mg Fe/m^3 (respirable fraction) and for zinc oxide is 2 mg/m^3 (respirable fraction). ACGIH has posted a Notice of Intended Change for copper,; the new proposed TLV is 0.1 mg.m^3 (inhalable fraction).

Acute Human Effects: Irritation

- *Dermal*

Lead and bismuth do not cause dermal irritation. Skin exposure to copper, iron, tungsten and zinc may cause dermal irritation.

- *Ocular*

Dusts of lead and all of the lead-free alternatives can cause ocular irritation, with the exception of zinc.

- *Respiratory*

Dusts of lead and zinc were not identified as respiratory irritants, while bismuth, copper, iron and tungsten can cause respiratory irritation.

Chronic Human Effects: Mutagenicity and Carcinogenicity
Lead is classified as both a mutagen and probable human carcinogen (IARC 2B). The lead-free alternatives in this assessment (bismuth, copper, iron, tungsten and zinc) are not classified as either mutagens or carcinogens.

Chronic Human Effects: Reproductive and Developmental Toxicity

Lead has been identified as a developmental toxicant in humans. Children are particularly sensitive to the chronic effects, which include slowed cognitive development and reduced growth. High lead exposure is also associated with reproductive effects, such as decreased sperm count in men, spontaneous abortions in women and low birthweight (United States Environmental Protection Agency (USEPA)

The lead-free alternatives in this assessment (bismuth, copper, iron, tungsten and zinc) have not been identified as reproductive or developmental toxicants.

Assessment Summary

Table 3.4.1 J summarizes the alternatives assessment information for lead ammunition.

Table 3.4.1 J: Assessment Summary – Alternatives for Lead Ammunition/ Shooting Ranges

Assessment Criteria		**Lead (Reference)**	**Comparison Relative to Lead**				
			Bismuth	**Copper**	**Iron**	**Tungsten**	**Zinc**
Technical/ Performance Criteria	Density	11.34 g/cm^3	-	-	-	+	-
	Frangibility	No	+	+	+	+	?
	Barrel Wear	Good	=	=	=	?	=
Environmental Criteria	Primary Drinking Water Standards (MCL Action Level)	15 µg/L	?	+	+	?	?
	Aquatic Toxicity: Water Quality Criteria (CMC)						
	Freshwater	65 µg/L	?	-	+	?	+
	Saltwater	210 µg/L	?	-	+	?	-
Human Health Criteria	Occupational Exposure: REL (8-hour TWA)	0.050 mg/m^3	?	+	+	+	+
	Carcinogenicity	EPA B2 IARC 2B	+	+	+	+	+
	Developmental Toxicity	Yes (Prop 65)	+	+	+	+	+
Cost	Cost/9mm round	$0.14-$0.20	-	-	-	-	-
	Operating Costs	High	+	+	+	+	+

Comparison Key + Better = Similar - Worse ? Unknown

3.4.2 Alternatives Assessment for Wheel Weights

Technical Assessment

Longevity/Life in Service

Wheel weights are installed on a vehicle's wheels during the tire balancing process and they typically remain in service until the tire is rebalanced or replaced, or until the wheel or vehicle is retired from use. Wheel weights are not typically reused so their life in service is determined by the frequency of tire rebalancing, the life of the tire and the life of the vehicle.

Wheel weights do not typically wear out but they can "fly off" when a vehicle is jarred or during sudden velocity changes. Factors such as improper installation and damage from contact with curbs or other objects can also cause weights to fall off. It is estimated that the annual loss rate is 10%. (Root 2000)

None of the reports and studies reviewed suggested that the material used for the weights affected the life of the weights or was a factor in the rate that the weights fall off the wheels.

Key Standards for Component/End-product

Wheel weights must meet the vehicle manufacturers' specifications before they can be used for Original Equipment Manufacturer (OEM) applications. OEM specifications can include the following: (Gearhart 2006b)

Corrosion protection: Corrosion protection is a focus of OEM specs. The OEMs typically require specs such as salt corrosion testing, cyclic corrosion testing, and UV testing for fading.

Physical dimensions: OEM specs limit maximum clearance dimensions (thickness, length, and width) to eliminate interference with other vehicle components and to prevent out-of-balance problems.

Shape: Some OEM specs specify shape properties such as curvatures or labeling surfaces.

Clip design: While the clip design is typically under producer control, the clip/weight assembly must meet specs such as clip gap and curl.

Material: OEMs did not specify the weight material in the past but they are beginning to specify lead-free weights.

Labeling: OEMs typically require labeling on wheel weights often including identification of the mass and material of the weight.

Aftermarket wheel weights are typically not required to meet OEM specifications.

Key Physical Characteristics & Performance Requirements

Density and Mass:

There are two common methods for attaching weights to wheels; clipping the weight to the rim of the wheel, and affixing the weight to the wheel using adhesive. For both wheel weight applications, a small weight size is desirable to prevent interference with other vehicle components, such as the brakes. Large weights are more visible and therefore less desirable, particularly for use on the outer rim of the wheel. Because density of the weight material directly influences the size of the wheel weight, it is a key physical characteristic.

All of the materials considered in this assessment are less dense than lead, which has a density of 11.34 g/cm^3. With a density of 8.96 g/cm^3, copper has the highest density of the alternatives in this assessment, followed by steel (7.87 g/cm^3), tin (7.34 g/cm^3), and zinc (7.10 g/cm^3). (Automation Creations) The density of a zinc alloy (ZAMAC) used for wheel weights is 6.76 g/cm^3. (Umicore)

The size (volume) of wheel weights made from copper, steel, tin and zinc must be larger than equivalent lead weights by 27%, 44%, 54%, and 60% respectively. Since the allowable thickness and width of wheel weights is limited, this increase in size is typically achieved by increasing the length of the weights. The mass of wheel weights used for passenger car applications typically ranges from 5 grams to 60 grams. (Hennessey Industries) Weights in this range are small enough that the increase in size (length) required for the alternative materials typically does not present problems. (Lohse, Sander & Wirts 2001)

Hardness:

Both clip-on weights and adhesive weights are mounted to curved surfaces of the wheel. Given the wide variety of wheel sizes and designs, it is desirable for wheel weights to be relatively soft and malleable so the curvature of the weight can be adjusted during installation to match the curvature of the wheel. (Lohse, Sander & Wirts 2001)Lead is a soft, malleable metal so it is relatively easy to make adjustments to the curvature of lead weights during installation with the use of a wheel weight hammer.

Lead has a hardness of 4.2 on the Brinell scale and a hardness of 1.5 on the Mohr's scale, which makes it softer than all of the alternative materials except pure tin. Pure tin has a Brinell hardness of 3.9 but some tin alloys are harder than lead (ASTM B 23 has a Brinell hardness of 17). The following table lists the wheel weight materials in order of increasing hardness: (Automation Creations)

Table 3.4.2 A: Hardness of Wheel Weight Materials

Material	Hardness		
	Brinell Scale	Mohr's Scale	Vickers Scale
Tin (pure)	3.9		
Lead	4.2	1.5	5
Tin (alloy)	17		
Zinc		2.5	30
Copper		3	50
ZAMAC (zinc alloy)	91		102
Steel (carbon)	170	5-6	

Malleability:

Copper, and tin are relatively malleable and the curvature of wheel weights made of these materials can be modified, to some degree, during installation. Zinc and zinc alloy are significantly harder and less malleable than lead so it may be difficult to adjust the curvature of the weights during installation. In addition to being relatively hard, steel has limited malleability and therefore forming of weights during installation to match the wheel diameter is typically not possible. The use of steel and zinc weights may require the number of standard wheel weight shapes to be increased. (Lohse, Sander & Wirts 2001)

Melting Point:

Heat generated during braking can result in brake disc temperatures of up to 1300 degrees F. The maximum temperature at the wheel rim where clip-on weights are installed is approximately 250 degrees F, while the maximum temperature at the wheel where adhesive weights are installed is typically well below 400 degrees F. (Lohse, Sander & Wirts 2001) The melting points for copper (1980 deg. F), steel (2732 deg. F), tin (450 deg. F) and zinc (787 deg. F) are higher than the maximum temperatures wheel weights are exposed to. The melting point of lead is 622 degrees F. (Automation Creations)

Corrosion Resistance:

Wheel weights must be corrosion resistant due to the harsh environment which includes exposure to moisture, high temperatures and road salt. The wheel weights must not undergo galvanic corrosion when affixed to steel or aluminum wheels. All lead weights used for OEM applications have a coating to prevent corrosion but many of the aftermarket lead weights are not coated. (Gearhart 2006a) Uncoated lead weights will leave black marks when applied to aluminum wheels.

Copper, steel and zinc wheel weights require a coating in order to prevent corrosion. Copper has good resistance to atmospheric corrosion but it develops a protective coating that over time thickens to give a green patina, which would be unacceptable for wheel weight applications. Steel weights will rust if they are not coated and zinc weights must be coated to prevent galvanic corrosion when mounted on aluminum wheels. A manufacturer of tin adhesive wheel weights states that no corrosion protection is required for tin wheel weights and that they will retain a good surface appearance. (Trax JH Ltd.)

Shape and Configuration:

It is advantageous for wheel weights to be malleable so they can be shaped during installation to match different wheel diameters. Using non-malleable materials for clip-on weights would result in the need to increase the number of shapes/styles/sizes to match the wide variety of wheel designs and sizes. The design of adhesive weights can be modified to account for the limited malleability of the materials like steel. Adhesive weights made of soft malleable materials can be in the form of a bar, while weights made of harder, less malleable materials are constructed of separate small weights attached to a strip of adhesive tape. Partitioning the weight into segments allows for application to the curved diameter of the wheel. (Lohse, Sander & Wirts 2001)

Recyclability:

Lead weights are collected for recycling after they are removed from wheels during the rebalancing of tires. The tire dealers and auto service stations that balance tires typically collect lead weights and send them to secondary smelters for recycling. EPA estimates that 16 million pounds of wheel weights are sent to secondary smelters. (USEPA 2005)

EPA estimates that an additional 8 million pounds may be processed in automobile recycling. During the recycling of automobiles, lead weights must be removed from the wheels to avoid contamination of recycled materials and auto shredder residue (ASR). (Ecology Center 2005a)

Lead from used wheel weights is also used by individuals who make their own lead fishing sinkers and ammunition, who collect the used weights from tire dealers and service stations. EPA estimates that 0.8 to 1.6 million anglers make their own fishing sinkers. This activity has the potential to expose individuals and family members to airborne lead particles or vapors released during the pouring of molten lead into the fishing sinker molds. (United States Environmental Protection Agency (USEPA) 1994)

All of the alternative materials considered in this assessment can also be recycled. Copper can be recycled without any loss of quality and the value of copper provides an economic incentive for recycling. The unique color and appearance of copper weights would facilitate material separation.

Copper recovered from refined or re-melted scrap composed 30% of the total U.S. copper supply. (Edelstein 2006)

Steel is easily recycled and material separation may be easier with steel weights since they can be identified and sorted with the use of magnets. The clips for clip-on weights are also made of steel and therefore could be recycled along with the weight, eliminating the need for separation. Steel weights do not need to be removed from steel wheels during automobile recycling.

Tin and zinc weights resemble lead weights and are more difficult to sort and separate. The high cost of tin provides an economic incentive to recover weights for recycling. A German study estimated that, when vehicles are dismantled for recycling, tin weights would be removed from the vehicles' wheels at a rate approaching 100% because the high price of tin would justify this procedure. (Lohse, Sander & Wirts 2001)

There is the potential that the challenge of separating lead-free weights from lead weights will result in a decline in the recycling of all wheel weights. (Ecology Center 2005b)

The following tables provide additional technical performance data for each of the alternatives.

Table 3.4.2 B: Wheel Weights – Copper

	Technical/ Performance Parameter	Measure/Metric	Source of Information
		Component/End-product	
	Key physical characteristics	Density: The density of copper is 8.96 g/cm^3 vs. 11.34 g/cm^3 for lead, which means that, for a given weight size (mass), a copper weight will be 27% larger volume than a lead weight. (MatWeb) Melting Point: At 1980° F, the melting point of copper is significantly higher than the 622° F melting point of lead and well above the maximum operating temperatures required for wheel weights. (MatWeb) Corrosion resistance: Copper has good resistance to atmospheric corrosion. However, it develops a protective coating that over time thickens to give a green patina, which would be unacceptable for wheel weight applications. Therefore, copper weights require a protective coating. (Corrosion Doctors) A manufacturer of copper adhesive wheel weights states that its copper weights are coated to meet OE standards. (Trax) Malleability: Like lead, copper is very malleable. Hardness: Annealed Copper, Vickers: 50 Lead, Brinell: 4.2 Lead, Vickers: 5 (MatWeb) Recyclability – Copper can be recycled without any loss of quality. Copper recovered from refined or remelted scrap composes 30% of the total U.S. copper supply.	MatWeb, 2006 Corrosion Doctors, 2006. Trax, 2006 Edelstein, 2006.

Table 3.4.2 C: Wheel Weights – Steel

	Technical/ Performance Parameter	Measure/Metric	Source of Information
	Component/End-product		
	Key physical characteristics	Density: The density of steel is approximately 7.87 g/cm^3 vs. 11.34 g/cm^3 for lead, which means that, for a given weight size (mass), a steel weight will be 44% larger volume than a lead weight. Melting Point: At 2732° F, the melting point of steel is significantly higher than the 621° F melting point of lead and well above the maximum operating temperatures required for wheel weights. Corrosion resistance: Steel weights are subject to rusting and therefore must be coated for all wheel weight applications to prevent corrosion. Hardness: Carbon steel, Brinell: 170 Lead, Brinell: 4.2 Lead, Vickers: 5 Malleability: Steel has limited malleability and therefore forming of the weights during installation to match the wheel diameter is not possible.	MatWeb, 2006

Table 3.4.2 D: Wheel Weights – Tin

	Technical/ Performance Parameter	Measure/Metric	Source of Information
	Component/End-product		
	Key physical characteristics	Density: The density of tin is 7.34 g/cm^3 vs. 11.34 g/cm^3 for lead, which means that, for a given weight size (mass), a tin weight will be 54% larger volume than a lead weight. (MatWeb) Melting Point: At 450° F, the melting point of tin is lower than the 622° F melting point of lead but it is above the maximum operating temperatures required for wheel weights. (MatWeb) Corrosion resistance: A manufacturer of tin adhesive wheel weights states that no corrosion protection is required for tin wheel weights and that they will retain a good surface appearance. (Trax) Hardness: 100% tin, Brinell: 3.9 tin alloy, ASTM B 23, Brinell: 17 Lead, Brinell: 4.2 Lead, Vickers: 5 (MatWeb)	MatWeb, 2006 Trax, 2006 Sander, 2000

Table 3.4.2 D: Wheel Weights – Tin

	Technical/ Performance Parameter	Measure/Metric	Source of Information
		Malleability: The malleability of tin is similar to lead. (Sander)	

Table 3.4.2 D: Wheel Weights – Zinc

	Technical/ Performance Parameter	Measure/Metric	Source of Information
Component/End-product			
	Key physical characteristics	Density: The density of zinc is 7.10 g/cm^3 vs. 11.34 g/cm^3 for lead, which means that, for a given weight size (mass), a zinc weight will be 60% larger volume than a lead weight. (MatWeb) The density of zinc alloy ZAMAC ZL5 is 6.76 g/cm^3. (Umicore) Melting Point: At 787° F, the melting point of zinc is significantly higher than the 622° F melting point of lead and well above the maximum operating temperatures for wheel weights. (MatWeb) Corrosion resistance: While zinc has good corrosion resistance, zinc wheel weights must be coated to prevent galvanic corrosion when mounted on aluminum wheels. (Umicore) Malleability: Zinc is malleable but is brittle at standard temperatures. Hardness: Zinc, Vickers: 30 ZAMAC ZL5, Brinell: 91 (Umicore) ZAMAC ZL5, Vickers: 102 (Umicore) Lead, Brinell: 4.2 Lead, Vickers: 5 (MatWeb)	MatWeb, 2006. Umicore, 2006.

Financial Assessment

Initial Purchase Price for Chemical/Alternative

Lead is significantly less expensive than any of the alternatives in this assessment, with the exception of steel. In December 2005, the Platts Metals Week North American producer price for lead was $0.65 per pound. The December 2005 price for copper (U.S. producer cathode) was $2.23 per pound. For tin (Metals Week composite), the price was $4.43 per pound, and for zinc (Platts Metals Week North American Special High Grade), the price was $0.88 per pound. Steel is not traded on an exchange (e.g. London Metals Market) but the price for hot rolled steel plate, which was $0.29 per pound in December 2005, suggests that the price of steel is competitive with lead. (Metals Consulting International (MCI))

Initial Purchase Cost for End-product/Component

There are a variety of factors that affect the price of wheel weights including: material, weight, type, quantity in package, order size, vendor, and whether the weight is uncoated or coated. Wheel weights for passenger cars are available in a variety of weights, typically ranging from 0.18 oz. to 2.1 oz.

Clip-on wheel weights are available in a variety of different styles, where each style is designed to fit a specific wheel rim design. Wheel rim designs can vary by the vehicle year, make and model and wheel weight manufacturers often provide tire dealers with a chart that matches the wheel weight style to the vehicle.. The wheel weight styles are designated by letter codes such as AW, EN, FN, LH, and MC. "P" type weights are generic weights for passenger cars and "T" type weights are for trucks. (Hennessey Industries)

For lead weights, the most significant price factor appears to be the coating. A coated lead weight can cost 2-3 times more than the uncoated equivalent. This can be illustrated using prices from an online auto parts retailer, Patchboy.com. The price for an uncoated 0.25 oz. AW type lead weight was $0.05, while the price for the coated version of the same weight was $0.16. The price for an uncoated 2 oz. AW type lead weight was $0.19, while the coated version of the same weight was $0.38. By contrast, the difference in price between the various types of weights is minimal. For example, for 0.25 ounce coated lead weights, there is a $0.01 difference between the AW type and the MC type. For the 2 ounce size, the prices for these two types are the same.

In a 2005 study, the Ecology Center of Ann Arbor, Michigan collected wheel weight price information from three retailers and three manufacturers located in North America, Europe and Japan. Price information was collected on clip-on lead weights (coated and uncoated) and clip-on coated steel and zinc weights. The Ecology Center made comparisons using the average price of weights from 0.25 – 2 oz. in size for each manufacturer and found that steel and zinc coated weights were comparable in price to lead coated weights. In some cases, lead-free weights could be purchased at a lower cost than high quality, coated lead weights. (Ecology Center 2005b)

The following table contains a cost comparison for lead, steel and zinc clip-on weights collected by the Ecology Center in 2005:

Table 3.4.2 E: Wheel Weight Cost Comparison

Average Cost per Weight (for weight sizes 0.25 – 2 ounce)

Source: Ecology Center, 2005b

Wheel Weight Description	Source	Approximate Average Weight Cost
Lead, uncoated, P style	Retailer "B"	$0.09
Steel, coated, P style	Manufacturer "E", Japan	$0.15
Lead, uncoated, MC style	Retailer "A"	$0.18
Zinc, coated, P style	Manufacturer "D", N. America	$0.24
Lead, coated, MC style	Retailer "B"	$0.25
Zinc, coated, MC style	Manufacturer "D", N. America	$0.26
Lead, coated, MC style	Retailer "C"	$0.29
Zinc, coated, MC style	Manufacturer "F", Europe	$0.32
Zinc, coated, MC style	Manufacturer "E", N. America	$0.38
Lead, coated, MC style	Retailer "A"	$0.43

Copper weights are high quality coated weights and appear to be marketed to high end autos including Aston Martin. (Trax JH Ltd.) Although pricing was not available, it is expected that copper weights are significantly more expensive than lead weights based on raw material costs.

Pricing for tin weights was not available. It is expected that tin weights are significantly more expensive than lead weights based on raw material costs.

Availability of Chemical/Alternative

The Ecology Center of Ann Arbor, Michigan has estimated that 70,000 tons of lead is used each year to manufacture wheel weights worldwide. However, the quantity of lead used for this application is decreasing as auto manufacturers are switching to steel and zinc weights.

In 2005, the worldwide mine production of copper was 16.4 million tons but strong demand in China and India resulted in a global production deficit. In 2006, increased capacity is expected to result in a modest production surplus. (Edelstein 2006)

Global crude steel output in 2005 was 1,129 million metric tons. (Iron and Steel Statistics Bureau (ISSB)) Increased production of steel wheel weights is not expected to affect supply or price of steel.

In 2005, the U.S. consumption of tin was 51,480 tons. Tin has not been mined in the United States since 1993. During the period of 2001-2004, the primary sources of imported tin were Peru (44%), China (14%), Bolivia (14%), and Indonesia (11%). World tin reserves appear to be adequate to meet foreseeable demand. Domestic demand for primary tin is expected to grow slowly in the next few years, at a rate of about 1% per year. That rate, however, could double in a few years if new applications, especially those in which tin is substituted for toxic materials, such as lead-free solders, find acceptance in the marketplace. (Carlin, James F. Jr 2006)

In 2005, there was a 200,000 ton production deficit of zinc worldwide. U.S. mine production in 2005 was 837,800 tons. Domestic zinc metal production capacity accounts for less than one-third of the quantity consumed domestically. Canada and Mexico are leading sources of zinc. (Gabby 2006)

Availability of Component/End-product

European and Japanese automobile manufacturers have switched to lead-free wheel weights and U.S. automobile manufacturers are currently in the process of making the switch. Most wheel weight manufacturers are now producing lead-free wheel weights to meet this demand. However, the aftermarket, which accounts for 80% of total wheel weight usage in the U.S., continues to use lead weights almost exclusively. (Gearhart 2006a)The following table lists the manufacturers known to produce lead-free wheel weights.

Table 3.4.2 F: Manufacturers of Lead-free Wheel Weights

Manufacturer	Country	Website	Type of Weight
Azuma	Japan	http://home1.catvmics.ne.jp/~azuma/	Steel
Banner GmbH	Austria	www.bannerbatterien.com	Steel, zinc
Dionys-Hoffman	Germany	www.dionys-hofmann.de	Zinc
Hennessy Industries, Inc. (Bada)	United States	www.ammcoats.com	Steel
Perfect Equipment	United States	www.perfectequipment.com	Steel, zinc
PCP Products	Thailand	www.pcproductsinter.com	Zinc
Plombco	Canada	www.plombco.com	Zinc
Trax JH Ltd.	United Kingdom	www.traxjh.com	Copper, steel, tin, zinc

Copper adhesive weights are available from at least one major wheel weight manufacturer but copper clip-on weights are not available. Copper is not currently being used in the U.S. for wheel weights by either the auto manufacturers or the aftermarket.

Steel wheel weights are available in both clip-on and adhesive styles. Steel is less dense than lead and therefore steel weights are larger than lead weights. As a result, size restrictions limit the availability of some steel weights. Steel weights are available for passenger vehicles which typically use .25 - 2 ounce weights. Trucks often require larger weights which may not be available in steel.

General Motors and Ford are in the process of converting to steel weights and it is expected that this conversion will be complete in 2006 and 2007 respectively. Asian auto manufacturers are currently equipping most of their vehicles with steel weights. (Gearhart 2006b)

The availability of tin wheel weights is very limited. Only one manufacturer (Trax) was identified as a producer of tin wheel weights and only in the adhesive style.

Many of the leading manufacturers of wheel weights, including at least two in North America, produce both adhesive and clip-on zinc weights. Zinc weights are available in a variety of sizes and types but the zinc product offerings are typically not as extensive as the lead product offerings. Zinc weights are used extensively in Europe. U.S. auto manufacturers are equipping new vehicles exported to Europe with zinc weights. (Ecology Center 2005a)

Capital Costs

A significant investment in production equipment is required to start-up production of lead-free wheel weights. Many of the major wheel weight manufacturers have already added lead-free wheel weight production capacity to meet the demand for lead-free weights from the auto manufacturers. However, manufacturers that supply the U.S. aftermarket must still produce lead weights to meet the ongoing demand for inexpensive weights. A shift by the aftermarket to lead-free weights would likely require manufacturers to make additional investments in capital equipment.

It is not known what the current production capacity is for lead-free weights or the capital costs required to convert lead weight production to lead-free weight production. It is also not clear whether one type of lead-free weight production process is more capital intensive than another.

Key Operating Costs During Use of End-product

Operating costs for lead-free wheel weights are expected to be the same as for the equivalent lead weights. Whether the lead-free weights are clip-on or adhesive weights, they are installed in the same manner as the equivalent lead weights.

Replacement Rate

The replacement rate of wheel weights is dependent on a number of factors, including the rate at which weights are lost, and the frequency of tire replacement. It is estimated that 10% of installed wheel weights are lost on an annual basis and the average lifespan of a tire is three years or 44,000 miles. (Ecology Center 2005b)

Key End-of-Product Life Costs

Lead wheel weights that are removed from wheels during tire balancing are subject to state and federal hazardous waste rules unless they are recycled. The lead waste is typically recycled at secondary lead smelters. The lead weights must be transported by licensed haulers, usually those that transport lead acid batteries. The removal and storage of lead weights for recycling may require special containers and recordkeeping. (Minnesota Pollution Control Agency (MPCA) 1998)

If lead weights are not removed from automobiles prior to automobile recycling and shredding, lead can contaminate other recyclable materials and the auto shredder residue (ASR). ASR contaminated with lead may be classified as hazardous waste. (Ecology Center 2005a)

Used copper, steel, tin and zinc wheel weights are not subject to state and federal hazardous waste rules and therefore waste management and recycling costs may be reduced. Steel, copper and zinc are widely used in automobiles so weights made from these materials are not likely to become contaminants in the automobile recycling process since they are recovered during the recycling process. The high value of scrap copper and tin provides an economic incentive for recovery and recycling.

The following tables provide additional financial data for each of the alternatives.

Table 3.4.2 G: Wheel Weights – Copper

	Financial Parameter	Measure/Metric	Source of Information
		Required Data	
	Initial purchase price for chemical/alternative	Copper raw material price: $2.23 per pound, U.S. producer cathode, December 2005 Lead raw material price: $0.65 per pound, Platts Metals Week North American producer price, December 2005	Edelstein, 2006 Gabby, 2006a
	Initial purchase cost for end-product/component	Copper weights are high quality weights with small size and appear to be marketed to high end autos including Aston Martin and although pricing was not available, it is expected that copper weights are significantly more expensive than lead weights.	Trax, 2006
	Availability of chemical/alternative	In 2005, the worldwide mine production of copper was 16.4 million tons but strong growth in China and India resulted in a global production deficit. In 2006, increased capacity is expected to result in a modest production surplus. It is estimated that 70,000 tons of lead are used per year to manufacture wheel weights worldwide.	Edelstein, 2006 Ecology Center, 2006
	Availability of component/end-product	Copper adhesive weights are available from at least one major wheel weight manufacturer. Copper is not currently being used in the U.S. for wheel weights by either the auto manufacturers or the aftermarket. The aftermarket, which accounts for 80% of wheel weight usage in the U.S., continues to use lead weights almost exclusively.	Trax, 2006 Gearhart, 2006a
		Additional Data if Available	
	Key operating costs during use of end-product	Operation costs for copper weights are expected to be the same as for other adhesive weights. Copper adhesive weights are installed in the same manor as other adhesive weights.	
	Key end-of-product life costs	Copper can be recycled without any loss of quality and 30% of U.S. demand is met by recycled copper. The price of copper provides an economic incentive to recycle scrap copper and it is expected that businesses that balance tires would recycle many of the copper weights removed from wheels. Identification of copper weights is not expected to be an issue since the weights are typically labeled and their copper color is unique.	Edelstein, 2006

Table 3.4.2 H: Wheel Weights – Steel

	Financial Parameter	Measure/Metric	Source of Information
		Required Data	
	Initial purchase price for chemical/alternative	The price for hot rolled steel plate in Dec 2005 was approximately $0.29/lb. Lead raw material price: $0.65 per pound, Platts Metals Week North American producer price, December 2005	steelonthenet, 2006 Gabby, 2006a
	Initial purchase cost for end-product/component	All steel wheel weights are coated. Steel clip-on weights are comparable in price to coated lead clip-on weights and in some cases they are lower in price. The average price for P style steel weights (0.25 – 2 oz.) from a Japanese manufacturer was $0.15.	Ecology Center, 2005b
	Availability of chemical/alternative	Global crude steel output in 2005 was 1,129 million metric ton. Increased production of steel wheel weights will not affect supply or price of steel. It is estimated that 70,000 tons of lead are used per year to manufacture wheel weights worldwide.	ISSB, 2006 Ecology Center, 2006
	Availability of component/end-product	Steel wheel weights are available in both clip-on and adhesive styles. Steel is less dense than lead and therefore steel weights are larger than lead weights. As a result, size restrictions limit the availability of some steel weights. Steel weights are available for passenger vehicles which typically use .25 - 2 ounce weights. Trucks often require larger weights which may not be available in steel. General Motors and Ford are in the process of converting to steel weights and it is expected that this conversion will be complete in 2006 and 2007 respectively. Asian auto manufacturers are currently equipping most of their vehicles with steel weights. In the U.S., the aftermarket, which accounts for 80% of wheel weight usage, continues to use lead weights almost exclusively.	Gearhart, 2006a
		Additional Data if Available	
	Key operating costs during use of end-product	Operation costs for steel weights are expected to be the same as for the equivalent lead weights since steel weights are installed in the same manor as lead weights.	
	Key end-of-product life costs	Used steel wheel weights are not subject to state and federal hazardous waste rules and therefore waste management and recycling costs may be reduced. Steel is widely used in automobiles so weights made from this material is not likely to become a contaminant in the automobile recycling process since it is recovered during the recycling process.	

Table 3.4.2 I: Wheel Weights – Tin			
	Financial Parameter	**Measure/Metric**	**Source of Information**
Required Data			
	Initial purchase price for chemical/alternative	Tin raw material price: \$4.43 per pound, Metals Week composite, December 2005 Lead raw material price: \$0.65 per pound, Platts Metals Week North American producer price, December 2005	Carlin, 2006b Gabby, 2006a
	Initial purchase cost for end-product/component	Pricing for tin weights was not available. It is expected that tin weights are significantly more expensive than lead weights.	
	Availability of chemical/alternative	In 2005, the U.S. consumption of tin was 51,480 tons. Tin has not been mined in the United States since 1993. World tin reserves appear to be adequate to meet foreseeable demand. Domestic demand for primary tin is expected to grow slowly in the next few years, at a rate of about 1% per year. That rate, however, could double in a few years if new applications—especially those in which tin is substituted for toxic materials, such as lead-free solders - find acceptance in the marketplace. Recycling: About 9,000 tons of tin from old and new scrap was recycled in 2005. Of this, about 5,000 tons was recovered from old scrap at 2 detinning plants and 91 secondary nonferrous metal processing plants. Import Sources (2001-04): Peru, 44%; China, 14%; Bolivia, 14%; Indonesia, 11%; and other, 17%. It is estimated that 70,000 tons of lead are used per year to manufacture wheel weights worldwide.	Carlin, 2006b Ecology Center, 2006
	Availability of component/end-product	Availability of tin wheel weights was very limited. In the U.S., the aftermarket, which accounts for 80% of wheel weight usage, continues to use lead weights almost exclusively.	Gearhart, 2006a
Additional Data if Available			
	Key operating costs during use of end-product	Operation costs for tin weights are expected to be the same as for the equivalent lead weights since tin weights are installed in the same manor as lead weights.	
	Key end-of-product life costs	Used tin wheel weights are not subject to state and federal hazardous waste rules and therefore waste management and recycling costs may be reduced. The high value of scrap tin provides an economic incentive for recovery and recycling.	

Table 3.4.2 J: Wheel Weights – Zinc

	Financial Parameter	Measure/Metric	Source of Information
	Required Data		
	Initial purchase price for chemical/alternative	Zinc raw material price: $0.88 per pound, Platts Metals Week North American Special High Grade, December 2005 Lead raw material price: $0.65 per pound, Platts Metals Week North American producer price, December 2005	Gabby, 2006b Gabby, 2006a
	Initial purchase cost for end-product/component	Coated zinc clip-on weights are comparable in price to coated lead clip-on weights. The average price for zinc weights (0.25 – 2 oz.) from a N. American manufacturer was approximately $0.24 for P style weights and $0.26 for MC style weights.	Ecology Center, 2005b
	Availability of chemical/alternative	U.S. mine production in 2005 was 837,800 tons. Domestic zinc metal production capacity accounts for less than one-third of quantity consumed domestically. Canada and Mexico are leading sources of zinc. In 2005, there was a 200,000 ton production deficit worldwide. It is estimated that 70,000 tons of lead are used per year to manufacture wheel weights worldwide.	Gabby, 2006b Ecology Center, 2006
	Availability of component/end-product	Many of the leading manufacturers of wheel weights, including at least two in N. America, produce zinc weights. Zinc weights are available in a variety of sizes and types but the manufacturers zinc product offerings are typically not as extensive as their lead product offerings. Zinc weights are used extensively in Europe. U.S. auto manufacturers are equipping new vehicles exported to Europe with zinc weights. In the U.S., the aftermarket, which accounts for 80% of wheel weight usage, continues to use lead weights almost exclusively.	Ecology, 2006 Gearhart, 2006a
	Additional Data if Available		
	Key operating costs during use of end-product	Operation costs for zinc weights are expected to be the same as for the equivalent lead weights since zinc weights are installed in the same manor as lead weights.	
	Key end-of-product life costs	Used zinc wheel weights are not subject to state and federal hazardous waste rules and therefore waste management and recycling costs may be reduced. Zinc is widely used in automobiles so weights made from this material is not likely to	

Table 3.4.2 J: Wheel Weights – Zinc			
	Financial Parameter	**Measure/Metric**	**Source of Information**
		become a contaminant in the automobile recycling process since it is recovered during the recycling process.	

Environmental Assessment

EPA estimates that 50 to 60 million pounds of lead are used each year to produce wheel weights in the United States. (United States Environmental Protection Agency (USEPA) 2005) In a 2003 study of the stocks and flows of lead wheel weights in the U.S., the U.S. Geological Survey (USGS) reported that approximately 56 million pounds of lead were used to produce wheel weights and approximately 130 million pounds of lead weights were in use on registered vehicles (Bleiwas, 2006). This USGS study estimated that 4 million pounds of lead wheel weights were lost on U.S. roadways in 2003 and an additional 8 million pounds were unaccounted for. The study also estimated that 75 percent (28 million pounds) of lead weights removed from vehicles by tire retailers, repair shops and dealerships were recycled and 6 million pounds of lead wheel weights were recycled by automotive scrap dealers in 2003.

A study published in 2000 estimated that the fleet of cars and light trucks currently in operation in the U.S. contain 55 million pounds of lead wheel weights. (Root 2000)Root estimated that 10% of these weights (5.5 million pounds) fall off the vehicles each year with 3.3 million pounds being deposited on urban streets where much of it is ground into dust by automobile traffic. The study claimed that the residual lead dust can then be washed into waterways or sewers, migrate into nearby residential properties, or become airborne particulates. Wheel weights are also collected during street cleaning operations and then disposed of in municipal landfills.

Drinking Water Standards

The fate of wheel weights that fall off during use is not fully understood but the potential for wheel weight materials to contaminate groundwater, including drinking water supplies, exists. Some of the wheel weights that are deposited on streets and highways are collected by street cleaning operations and disposed of in municipal landfills. The acidic conditions in the municipal landfills can solubolize lead from the wheel weights, resulting in lead contamination of groundwater. (United States Environmental Protection Agency (USEPA)

The National Primary Drinking Water Regulations are legally enforceable standards, set by EPA, that apply to public water systems. In these standards, the Maximum Concentration Level (MCL) for lead in drinking water is 15 μg/L and the Maximum Concentration Level Goal (MCLG) is zero. Copper is the only alternative wheel weight material in this assessment for which EPA has set an MCL. Copper has an MCL of 1300 μg/L.

EPA has also established National Secondary Drinking Water Standards, which are non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water. The following list shows the alternative wheel weight materials included in these secondary standards (aluminum is used in the zinc alloy ZAMAC):

- Copper: 1000 μg/l
- Iron: 300 μg/l

- Zinc: 5000 μg/l
- Aluminum: 20-500 μg/l

Florida and Minnesota have established maximum concentration levels for tin in drinking water (4200 μg/l and 4000 μg/l respectively). Arizona set the maximum concentration level for copper at 1300 μg/l.

Affinity for Water: Water Solubility

Lead, copper, steel and tin are insoluble in water. Zinc is soluble in water but the solubility is dependent on the properties of the water, such as acidity, temperature, chlorine concentration and hardness. It should be noted that certain compounds of these metals may be soluble.

Density

All of the materials considered in this assessment are less dense than lead, which has a density of 11.34 g/cm^3. With a density of 8.96 g/cm^3, copper has the highest density of the alternatives in this assessment, followed by steel (7.87 g/cm^3), tin (7.34 g/cm^3), and zinc (7.10 g/cm^3). (Automation Creations)The density of a zinc alloy (ZAMAC) used for wheel weights is 6.76 g/cm^3. (Umicore)

Bioaccumulation

According to the International Chemical Safety Cards (ICSCs), bioaccumulation of lead may occur in plants and mammals and it is strongly advised that lead does not enter the environment. Specific information on the bioaccumulation of copper, steel, tin, and zinc were not available. As discussed earlier in this report, EPA is in the process of developing a framework that will address the issue of bioaccumulation of metals, as well as related issues such as bioavailability.

Aquatic toxicity

National Recommended Water Quality Criteria was used as a source for data on aquatic toxicity of lead and lead-free alternatives. Water Quality Criteria includes the following two aquatic life criteria for both freshwater and saltwater:

- Criteria Maximum Concentration (CMC) – An estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.
- Criteria Continuous Concentration (CCC) – An estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

Lead, copper and zinc are listed as Priority Toxic Pollutants and iron is listed as a Non Priority Pollutant. Tin was not included in the Water Quality Criteria list. The following table shows the Water Quality Criteria for lead, copper, iron and zinc.

Table 3.4.2 K: Water Quality Criteria

	Freshwater		Saltwater	
Priority Pollutant	**CMC (µg/L)**	**CCC (µg/L)**	**CMC (µg/L)**	**CCC (µg/L)**
Lead	65	2.5	210	8.1
Copper	13	9.0	4.8	3.1
Iron	-	1000	-	-
Zinc	120	120	90	81

The Water Quality Criteria values indicate that lead, copper and zinc are toxic to aquatic organisms, even at relatively low concentrations. Of the wheel weight materials considered in this assessment, tin and steel appear to be the least toxic to aquatic organisms.

In 1994, EPA addressed the aquatic toxicity of alternatives to lead fishing sinkers in its response to citizens' petition and proposed ban for lead fishing sinkers. In its assessment of aquatic toxicity of lead alternatives, EPA made the following statements about copper, tin and zinc: "Laboratory studies indicate that copper is more toxic to aquatic organisms, such as fish, crustaceans, worms, and algae than lead." (United States Environmental Protection Agency (USEPA) 1994) However, EPA believes that environmental conditions in freshwaters would mitigate the toxicity of copper to aquatic organisms. "Tin, in the inorganic form, is generally much less toxic to aquatic organisms (crustaceans and fish) than lead because of its low solubility, poor absorption, low uptake rate, and rapid excretion." Zinc is more toxic to aquatic organisms (fish and crustaceans) than lead and it may be more bioavailable to aquatic organisms than lead. Information about the aquatic toxicity of steel was not found.

Human Health Assessment

Acute Human Effects

Occupational Exposure Limits

IDLH

The Immediately Dangerous to Life or Health Concentrations (IDLH) for lead is 100 mg/m^3. The IDLH for copper and tin is also 100 mg/m^3. Data on the IDLH for steel and zinc were not located. For iron, 1-2 grams may cause death but 2-10 is usually ingested in fatal cases.

PEL

The Permissible Exposure Level (PEL) for lead is 0.050 mg/m^3 (8-hour TWA). The PEL (TWA) for copper is 1 mg/m^3; for tin it is 2 mg/m^3; and for aluminum (in zinc alloy ZAMAC) it is 15 mg/m^3. PELs have not been established for steel and zinc; however, PELs have been set for zinc chloride (1 mg/m^3) and zinc oxide (5 mg/m^3).

REL

The Recommended Exposure Level (REL) for lead is 0.050 mg/m^3 (TWA). The REL (TWA) for copper is 1 mg/m^3; for steel (iron) it is 1 mg/m^3; for tin it is 2 mg/m^3; and for aluminum (in zinc alloy ZAMAC) it is 10 mg/m^3 (total). An REL has not been established for zinc.

Irritation

Dermal

Lead does not cause dermal irritation. Skin exposure to copper, steel (iron), tin and zinc may cause dermal irritation.

Ocular

Dusts of lead and all of the lead-free alternatives can cause ocular irritation, with the exception of zinc.

Respiratory

Dusts of lead and zinc were not identified as respiratory irritants, while copper, steel (iron) and tin can cause respiratory irritation.

Chronic Human Effects

Mutagenicity and Carcinogenicity

Lead is classified as both a mutagen and probable human carcinogen (IARC 2B). The lead-free alternatives in this assessment (copper, steel, tin and zinc) are not classified as either mutagens or carcinogens.

Reproductive and Developmental Toxicity

Lead has been identified as a developmental toxicant in humans. Children are particularly sensitive to the chronic effects, which include slowed cognitive development and reduced growth. High lead exposure is also associated with reproductive effects, such as decreased sperm count in men, spontaneous abortions in women and low birth weight (USEPA).

The lead-free alternatives in this assessment (copper, steel, tin and zinc) have not been identified as reproductive or developmental toxicants.

Assessment Summary

The following is a summary of the alternatives assessment data for lead wheel weights.

Table 3.4.2 L: Assessment Summary Alternatives for Lead Wheel Weights

Assessment Criteria		Lead (Reference)	Comparison Relative to Lead			
			Copper	Steel	Tin	Zinc
Technical/ Performance Criteria	Density	11.34 g/cm^3	-	-	-	-
	Malleability	Good	=	-	=	-
	Corrosion Resistance (with coating)	Good	=	=	+ (coating not required)	=
Environmental Criteria	Primary Drinking Water Standards (MCL Action Level)	15 □g/l	+	+ (iron)	+ (FL & MN)	?
	Aquatic Toxicity: Water Quality Criteria (CMC) Freshwater Saltwater	65 □g/L 210 □g/L	- -	+ (iron) ?	? ?	+ -
Human Health Criteria	Carcinogenicity	EPA B2 IARC 2B	+	+	+	+
	Developmental Toxicity	Yes (Prop 65)	+	+	+	+
	Occupational Exposure: REL (8-hour TWA)	0.050 mg/m^3	+	+	+	+
Cost	Price per weight (coated, ¼ – 2 oz)	$0.25 - $0.43	-	= / +	-	=
	Available in clip-on & adhesive styles	Yes	-	=	-	=
	End-of-Life Cost (Auto Shredder)	Average	+	+	+	+

Comparison Key + Better = Similar - Worse ? Unknown

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3.4.3 Alternatives Assessment for Fishing Sinkers

Technical Assessment

Longevity/Life in Service

The primary factor affecting the life in service of fishing sinkers is the frequency that they are lost during use. Fishing sinkers of all types are lost during use, such as when the sinker becomes caught on weeds, rocks or other objects. Fishing sinkers can also come loose during casting if they are not properly secured.

Fishing sinkers do not typically wear out. A review of literature on fishing sinkers in the environment, as well as fishing sinker manufacturers' and retailers' websites and brochures, did not identify any data about the service life of fishing sinkers or the effect that the materials of construction have on the service life.

Key Standards for Component/End-product

In efforts to protect water birds from lead poisoning from fishing sinkers, the following northeastern states have enacted legislation restricting the use and/or sale of certain lead fishing sinkers (Minnesota Office of Environmental Assistance (MOEA)):

- Massachusetts - In June 2000, the Massachusetts Fisheries & Wildlife Board voted to prohibit the use of all lead sinkers for the taking of fish in Quabbin and Wachusett Reservoirs, the two bodies of water that support the core of that state's loon population.
- Maine - Passed legislation in 2001 (effective January 1, 2002) to ban the sale of lead sinkers weighing ½ oz or less.
- New Hampshire - Legislation passed in 1998 (effective in 2000) prohibits the use of lead sinkers up to 1 oz and lead jigs up to 1 in. in length in the state's lakes and ponds. N.H. later expanded the legislation to include all waters of the state. Starting January 1, 2006, the sale of lead sinkers weighing 1 oz or less and lead jigs less than 1 in. long along their longest axis are prohibited in New Hampshire.
- New York - Passed legislation in 2002 (effective May 2004) that bans the sale of lead sinkers ½ oz or less to the end user.
- Vermont - Passed legislation in 2004 banning the sale of lead sinkers weighing ½ oz or less (effective January 2006), and the use of those lead sinkers (effective January 2007) in the state.

The U.S. Fish and Wildlife Service banned lead sinkers in two national wildlife refuges and Yellowstone National Park. It is currently discussing restrictions on the use of lead sinkers and jigs at other national wildlife refuges where loons and trumpeter swans breed. Great Britain banned the use of lead sinkers in 1987. In Canada, it is illegal to use lead fishing sinkers and jigs in national parks and national wildlife areas (United States Fish & Wildlife Service (USFWS); New Hampshire Fish and Game Department).

Key Physical Characteristics and Key Performance Requirements

Fishing sinkers are available in a wide variety of styles, sizes, and configurations where each type is designed to meet the requirements of the application or the preference of the user. The ideal physical characteristics for fishing sinker materials depend, to a large degree, on the intended application of the sinker. A review of manufacturers' and retailers' literature and websites and online product reviews indicates that key physical characteristics of fishing sinker materials include: density, malleability, brittleness, corrosion resistance, and hardness. It is estimated that 0.8 – 1.6 million anglers in the U.S. produce their own lead sinkers (United States Environmental Protection Agency (USEPA) 1994)for these individuals who mold their own fishing sinkers, the melting point of the material is also important.

It should be noted that optimal characteristics for fishing sinker materials vary according to application and user preference. For example, malleability and softness are desirable characteristics for split-shot sinkers while hardness is a desirable characteristic for other types of sinkers, since hard materials make noise that is said to attract fish.

Split-shot sinkers are one of the most common types of fishing sinkers. They come in sizes ranging from BB size (0.44 cm in diameter) to about the size of a raisin. The "split" refers to the groove where the fishing line is inserted. The sinker is secured to the line by crimping which closes the groove onto the line. Removable split-shot sinkers feature wings, that when squeezed, open the groove releasing the fishing line. A description of other fishing sinker types can be found in an article by Tim Allard, "An Introduction to Fishing Sinkers" (Allard).

Density and Mass:

Fishing sinkers have two primary purposes: 1) to provide mass to the fishing line to achieve improved casting distance and accuracy and; 2) to provide mass to the fishing line so the bait stays in the desired location (USEPA 1994; McMahon 2006a). The sinker must be made of a material that provides sufficient mass to achieve these results. For some applications, smaller sinkers are desirable because they are less likely to get hung up on obstacles and less likely to be seen by the fish. For other applications, an increase in the sinker size can reduce snags because larger sinkers slide over cracks that smaller sinkers could get caught in (McMahon 2006b).

Ceramic is the least dense material considered in this assessment. With a density of 2.6 g/cm^3 (Du-Co, 2006), a ceramic sinker must be more than three times the volume of a lead sinker in order to achieve a given mass. While a larger sinker may be desirable for some applications, the low density of ceramic is a drawback for use in other applications.

The densities of tin (7.34 g/cm^3), steel (7.87 g/cm^3), and bismuth (9.8 g/cm^3) are all less than that of lead (11.34 g/cm^3) (MatWeb 2006). For bismuth sinkers, a relatively small increase in volume (16%) will achieve the same mass as a lead sinker. Steel and tin sinkers must be 44% and 54% larger in volume respectively than lead sinkers for a given mass. For many applications, these differences in sizes are not significant enough to affect performance.

The density of tungsten (19.3 g/cm^3) is significantly higher than lead and therefore, for a given mass, tungsten sinkers are 41% smaller in volume than lead sinkers for a given mass, which is desirable for applications that benefit from small sinker size (Automation Creations).

Hardness:

The hardness of a sinker can affect performance in several ways. Sinkers made from hard materials are less likely to deform when they hit rocks or other hard objects. Hard sinkers also make more noise when they contact rocks or other hard objects, which is desirable because the noise can attract fish. Some manufacturers and anglers claim that sinkers made of hard materials provide anglers with a better feel for the lake or river bottom than sinkers made of softer materials like lead. Hard sinkers may be more snag-resistant in some cases since they tend to bounce off a snag. (Ellis)

Lead has a hardness of 4.2 on the Brinell scale and a hardness of 1.5 on the Mohr's scale, which makes it softer than all of the alternative materials except pure tin. Pure tin has a Brinell hardness of 3.9 but some tin alloys are harder than lead (ASTM B 23 has a Brinell hardness of 17). Bismuth and tin alloy are somewhat harder than lead while ceramic, steel and tungsten sinkers are significantly harder than lead. Table 3.4.3A lists the fishing sinker materials in order of increasing hardness (Automation Creations):

Table 3.4.3 A: Relative hardness of candidate sinker materials.

Material	Hardness	
	Brinell Scale	Mohr's Scale
Tin (pure)	3.9	
Lead	4.2	1.5
Bismuth	7	
Tin (alloy)	17	
Steel (stainless)	123	5-6
Tungsten	294	7
Ceramic		7.5

Malleability

An advantage of using soft, malleable materials for fishing sinkers is that they can be used for fishing sinker applications where the sinker is crimped onto the fishing line, such as the commonly used split-shot sinkers. Lead is a soft, malleable metal, which makes it ideal for these types of fishing sinkers.

Bismuth is malleable but it is relatively brittle and therefore would be likely to crack if used for split-shot sinkers or other types that utilize crimping (Automation Creations). Ceramic is not malleable and is relatively brittle so it is not a candidate for sinkers that are crimped. Steel and tungsten are not used for split-shot sinkers due to their limited malleability. Tin is malleable like lead and frequently used for split-shot applications. However, tin is more brittle than lead and in a review of lead-free sinkers, it was noted that this brittleness can cause tin split-shot sinkers to fail, particularly if the sinkers are reused (Ellis).

Corrosion Resistance:

Corrosion resistance is a key physical characteristic of fishing sinkers due to their exposure to harsh elements such as seawater. Lead, bismuth, ceramic, stainless steel, tin, and tungsten are corrosion resistant materials and are successfully used for fishing sinkers without corrosion preventive coatings or special treatment. Carbon steel sinkers will rust unless they are coated (Ellis).

Melting Point:

The relatively low melting point of lead (622° F) makes it possible for individuals to mold their own lead sinkers at home. The molds and melting pots used for home production of lead sinkers are available through retailers that sell fishing supplies (Brooks, 2005). The low melting points for both bismuth (520° F) and tin (450° F) make home production of fishing sinkers a possibility. The high melting point of steel (2732° F) and tungsten (6100° F) prohibit home molding of sinkers with these materials. The production of ceramic products requires firing at temperatures exceeding 1400° F, so home production of ceramic sinkers would not be feasible.

Shape and Configuration:

There are a wide variety of shapes, sizes and styles of sinkers, each of which are designed to meet specific requirements. Fishing sinker requirements are dependent on a wide variety of factors including: type of fish, type of bait, water conditions, fishing technique, and user preference. To meet these requirements, the sinkers must be available in a variety of shapes and weights. For example, sinkers with rounded or tapered shapes (*e.g.,* bullet or egg sinkers) are designed to resist snags and slip through weeds. Sinkers with flat edges (*e.g.,* pyramid sinkers) are designed to dig into soft bottoms or stay in place in fast currents (Allard).

Fishing sinkers are attached to the fishing line using a variety of techniques including crimping on the line, tying to a loop on the sinker, or, for slip-sinkers, threading the line through the hole in the center of the sinker. Sinkers that are crimped onto the line must be made from a malleable material which does not break when crimped. The sinker must not cut into or abrade the fishing line.

Bismuth sinkers may be manufactured using a molding process similar to lead sinkers; however, bismuth expands as it solidifies and therefore may require the use of high-quality milled molds (Scheuhammer, Norris 1995). The physical properties may limit the variety of bismuth sinker shapes and configurations. Bismuth is relatively brittle and cannot be used for split-shot sinkers or other sinkers where crimping is required because its brittleness results in breakage when it is crimped onto the fishing line.

Ceramic sinkers are currently only available in limited configurations and sizes (i.e. slip sinkers) (Big Ten Tackle). It is not clear whether this is a function of market demand or a limitation of the manufacturing process and/or material properties. The hardness and brittleness of ceramic eliminate the possibility of ceramic being used for split-shot sinkers or other sinkers where crimping is required.

Most steel sinkers are manufactured using a machining process rather than a molding process and therefore the available shapes and configurations are more limited than lead sinkers. Steel can be machined into the symmetrical shape of egg sinkers and bullet or worm weights but machining steel into pyramid or other flat sided weights is probably not feasible. The hardness and limited malleability of steel eliminate the possibility of steel being used for split-shot sinkers or other sinkers where crimping is required.

Like lead, tin sinkers can be produced using a molding process and tin is widely used as a substitute for lead for split-shot sinkers.

Pure tungsten can be forged or extruded; however, impure tungsten is brittle and is difficult to work (ChinaTungsten Online Manufacturing & Sales Corporation). Tungsten is also a very hard metal. These factors may limit the shapes and configurations for tungsten sinkers. Tungsten can be used in a composite material, such as tungsten powder in a polymer base, which could increase the options available.

Appearance*:*

Unnatural appearance, such as having a shiny surface, can be a negative, particularly in clear water situations (Ellis). A shiny, bright surface can be a positive in some applications. Steel and tungsten sinkers can be produced with shiny, bright surfaces. Steel sinkers can be painted a variety of colors to attract fish and paint adheres to steel better than lead. Steel sinkers can also be impregnated with a long-lasting scent designed to attract fish or mask undesirable human odors (Duke).

Ceramic sinkers have the advantage of blending in with a river or lake bottom (Big Ten Tackle). Tin split-shot sinkers are shinier than lead, which could be a negative factor in clear-water situations (Ellis).

Tables 3.4.3 B-F provide additional technical performance data for each of the alternatives.

Table 3.4.3 B: Fishing Sinkers – Bismuth

	Technical/ Performance Parameter	Measure/Metric	Source of Information
Component/End-product			
	Key physical characteristics	Density: The density of bismuth is approximately 9.8 g/cm^3 vs. 11.34 g/cm^3 for lead, which means that, for a given sinker size (mass), a bismuth sinker will be 16% larger volume than a lead sinker. (MatWeb) Melting Point: At 520° F, the melting point of bismuth is lower than the 622° F melting point of lead. (MatWeb) Malleability: Bismuth alloys are relatively malleable, similar to lead. (MII) Brittleness: Bismuth is relatively brittle for a metal. (MII) Corrosion resistance: Bismuth does not corrode in the atmosphere unless attacked by strong acids. (MII) Hardness: Bismuth, Brinell: 7 Lead, Brinell: 4.2 Lead, Vickers: 5 (MatWeb)	MatWeb, 2006 MII, 2006

Table 3.4.3 C: Fishing Sinkers – Ceramic

	Technical/ Performance Parameter	Measure/Metric	Source of Information
Component/End-product			
	Key physical characteristics	Density: The density of ceramic is 2.6 g/cm^3 vs. 11.34 g/cm^3 for lead, which means that, for a given weight size (mass), a ceramic sinker will be more than 3.3 times larger volume than a lead sinker. Hardness: Ceramic, Mohr's Scale: 7.5 (Du-Co) Lead, Mohr's Scale: 1.5 Lead, Brinell: 4.2 Lead, Vickers: 5 (MatWeb)	Du-Co

Table 3.4.3 D: Fishing Sinkers – Steel

	Technical/ Performance Parameter	Measure/Metric	Source of Information
Component/End-product			
	Key physical characteristics	Density: The density of steel is approximately 7.87 g/cm^3 vs. 11.34 g/cm^3 for lead, which means that, for a given	Ellis, 2006

Table 3.4.3 D: Fishing Sinkers – Steel

	Technical/ Performance Parameter	Measure/Metric	Source of Information
		weight size (mass), a steel sinker will be 44% larger volume than a lead sinker. (MatWeb) Melting Point: At 2732 °F, the melting point of steel is significantly higher than the 621 °F melting point of lead. (MatWeb) Corrosion resistance: Sinkers made from carbon steel are subject to rusting and therefore must be coated to prevent corrosion. Stainless steel is corrosion resistant and would not require coating. (Ellis) Malleability: Steel has limited malleability. Hardness: Stainless Steel (304), Brinell: 123 Stainless Steel (304), Vickers: 129 Steel, Mohr's Scale: 5 Lead, Mohr's Scale: 1.5 Lead, Brinell: 4.2 Lead, Vickers: 5 (MatWeb)	MatWeb, 2006

Table 3.4.3 E: Fishing Sinkers – Tin

	Technical/ Performance Parameter	Measure/Metric	Source of Information
		Component/End-product	
	Key physical characteristics	Density: The density of tin is 7.34 g/cm^3 vs. 11.34 g/cm^3 for lead, which means that, for a given weight size (mass), a tin weight will be 54% larger volume than a lead weight. (MatWeb) Melting Point: At 450° F, the melting point of tin is lower than the 622° F melting point of lead. (MatWeb) Corrosion resistance: Tin is corrosion resistant and because of this property it is commonly used to coat steel to produce tinplate, which is used for food packaging applications. Malleability: The malleability of tin is similar to lead. (Sander) Brittleness: In a review of lead-free sinkers, one angler stated that the brittleness of tin can result in split-shot splitting apart, particularly if the tin split-shot is reused. (Ellis) Hardness:	MatWeb, 2006 Ellis, 2006 Sander, 2000

Table 3.4.3 E: Fishing Sinkers – Tin

	Technical/ Performance Parameter	Measure/Metric	Source of Information
	Component/End-product		
		100% tin, Brinell: 3.9 Tin alloy, ASTM B 23, Brinell: 17 Lead, Brinell: 4.2 Lead, Vickers: 5 (MatWeb)	

Table 3.4.3 F: Fishing Sinkers – Tungsten

	Technical/ Performance Parameter	Measure/Metric	Source of Information
	Component/End-product		
	Key physical characteristics	Density: The density of tungsten is 19.3 g/cm^3 vs. 11.34 g/cm^3 for lead, which means that, for a given weight size (mass), a tungsten weight will be 41% smaller volume than a lead weight. (MatWeb) Melting Point: At 6100° F, the melting point of tungsten is significantly higher than the 622° F melting point of lead. (MatWeb) The high melting point of tungsten eliminates the possibility of anglers molding their own sinkers. The high temperatures result in higher energy costs during manufacturing. The high temperatures can also cause production delays when material or mold changes are made since the molds can take up to two days to cool. Corrosion resistance: Lead and tungsten are corrosion resistant materials and are successfully used for fishing sinkers without corrosion preventive coatings or special treatment. Malleability: Tungsten is very hard (Brinell hardness of 294) and has limited malleability (MatWeb). Hardness: 100% tungsten, Brinell: 294 100% tungsten, Vickers: 310 Tungsten, Mohr's Scale: 7 Lead, Mohr's Scale: 1.5 Lead, Brinell: 4.2 Lead, Vickers: 5 (MatWeb)	MatWeb, 2006

Financial Assessment

Initial Purchase Price for Chemical/Alternative

Lead has the advantage of being a relatively inexpensive metal. A major U.S. fishing sinker manufacturer (Water Gremlin) said that its cost to purchase lead was $0.30/lb in 2003. In 2003, the Platts Metals Week average North American Producer price was $0.4/lb. In December 2005, the Platts Metals Week North American producer price was $0.65/lb.

In 2005, the dealer prices for bismuth fluctuated from an average of $3.55/lb in the first quarter to an average of $4.57/lb in the fourth quarter. The 2005 fourth quarter price represented a 33% increase over the 2004 fourth quarter price. Ceramic sinkers cost 33% more per pound than lead according to a manufacturer of ceramic sinkers (Big Ten Tackle). Steel is not traded on an exchange (e.g. London Metals Market) but the price for hot rolled steel plate, which was $0.29/lb in December 2005, suggests that the price of steel is competitive with lead. The Platts Metals Week average composite price for tin in December 2005 was $4.43/lb, which was 7% higher than the November price and 20% less than the December 2004 price. Tungsten prices fluctuated from approximately $2.72/lb in January 2005 to approximately $9.98/lb in May 2005 (DesLauriers 2005).

Initial Purchase Cost for End-product/Component

Results of an economic analysis conducted by EPA in 1994 indicated that a federal ban on the manufacture and distribution of lead and zinc fishing sinkers (1 in. or less in any dimension) would increase the average costs to individual anglers by only $1.50 -3.50/y (USEPA 1994). A study conducted in 1991 found that anglers in Canada spent approximately $500/y on their sport (Filion et al. 1991). While these studies were conducted more than a decade ago, they suggest that fishing sinker purchases represent less than 1% of total expenditures by anglers on their sport.

Fishing sinker cost data for this assessment was collected from three online retailers (Cabela's, Bass Pro Shops, FishUSA.com) and a retail store (Wal-Mart) that carry fishing supplies. Cost data were limited to common types of fishing sinkers used for freshwater fishing, including egg and slip sinkers, split-shot, worm and bullet weights. The cost data were limited to sinkers 1-1/2 oz and less. Wherever possible, price comparisons were made between lead and lead-free sinkers available at the same retailer.

Bismuth egg sinker prices are approximately 5 to 6 times the price of lead egg sinkers, while bismuth worm weights are approximately 4 to 6 times the price of lead worm weights. Ceramic slip sinker prices are approximately 2 to3 times the price of lead slip sinkers. Tin removable split shot sinker prices are approximately 1.5 to 4 times the price of lead removable split shot sinkers. Tungsten bullet and worm weight prices are approximately 7 to 12 times the price of lead bullet weights. Tungsten drop shot weight prices are approximately 3 to 7 times the price of lead drop shot weights.

Steel fishing sinkers appear to be the most competitively priced lead-free alternative. Steel bullet weight prices are approximately 1 to 2 times the price of lead bullet weight sinkers and steel egg sinkers are 0.7 to 2 times the price of lead egg sinkers.

The lead-free fishing sinkers were typically sold in packages with smaller quantities of sinkers than the equivalent lead sinkers, which may affect a per unit price comparison.

Availability of Chemical/Alternative

It is estimated that 2,450 metric tons of lead are used each year in the United States to produce approximately 477 million fishing sinkers (USEPA 1994)

Bismuth, tin, and tungsten are relatively scarce metals with a limited reserve base, while iron (steel) is more abundant than lead (European Commission Enterprise Directorate-General 2004).

All primary bismuth consumed in the U.S. is imported and less than 5% is obtained by recycling old scrap. Most bismuth is produced from mines in Mexico, China, Peru and Bolivia. It is a byproduct of processing lead ores, and in China, it is a byproduct of tungsten ore processing. Reported bismuth consumption was 2,120 metric tons in 2003 in the U.S. Worldwide demand is growing at about 5% per year, driven in part by its use as a replacement for lead but a global shortage is not expected. However, the supply could be constrained by low prices (Carlin, James F. Jr.).

Availability of steatite ceramic would not be affected by increased production of ceramic sinkers. Talc, including the steatite used to produce this ceramic, is mined in many countries including the U.S. and is used in a wide variety of products, including paper, talcum powder, paint filler, and ceramic products such as electrical insulators. U.S. mines produced around 1 million metric tons of crude talc ore per year during the 1990's (United States Geological Survey (USGS) 2000).

Global crude steel output in 2005 was 1,129 million metric tons (Iron and Steel Statistics Bureau (ISSB)). Given the availability and wide use of steel, increased production of steel fishing sinkers are not likely to affect the supply or price of steel.

In 2005, the U.S. consumption of tin was 51,480 tons. Tin has not been mined in the United States since 1993. During the period of 2001-2004, the primary sources of imported tin were Peru (44%), China (14%), Bolivia (14%), and Indonesia (11%). World tin reserves appear to be adequate to meet foreseeable demand. Domestic demand for primary tin is expected to grow slowly in the next few years, at a rate of about 1% per year. That rate, however, could double in a few years if new applications, especially those in which tin is substituted for toxic materials, such as lead-free solders, find acceptance in the marketplace (Carlin, James F. Jr 2006).

U.S. consumption of tungsten in 2005 was 11,600 metric tons. World tungsten supply is dominated by Chinese production and exports. The Chinese government regulates tungsten production and the total volume of tungsten exports, and the government has gradually shifted the balance of export quotas towards value-added downstream tungsten materials and products. In 2005, inadequate supplies of tungsten concentrates within China combined with increased demand for tungsten materials in China and elsewhere resulted in steep increases in the prices of tungsten concentrates. In response to this price increase, the sole Canadian tungsten mine restarted operations and action was taken to develop tungsten deposits or reopen inactive tungsten mines in Australia, China, Peru, Russia, the United States, and Vietnam (Shedd 2006).

Availability of Component/End-product

The availability of lead-free sinkers was assessed by determining the products carried by three major online retailers (Cabela's, Bass Pro Shops & FishUSA.com) and Wal-Mart stores.

Lead split-shot sinkers account for almost half of the total lead sinker market and 68% of lead sinkers 1 in. in size or less (USEPA 1994). Tin is the only readily available lead-free material used for split-shot sinkers, since most other materials are too hard and/or brittle for this application.

Bismuth sinkers are available in egg sinker and worm weight styles. Ceramic sinkers were not available at three major online retailers (Cabela's, Bass Pro Shops & FishUSA.com) or at Wal-Mart stores. An internet search located only one company selling ceramic sinkers and the selection was limited to two sizes of slip sinkers. Steel bullet weights and egg sinkers were available at two major online retailers (Cabela's & Bass Pro Shops). A Wal-Mart store did not carry steel sinkers.

Capital Costs and Key Manufacturing Costs for Component/End-product

It is possible to switch existing lead sinker production equipment to manufacture sinkers out of materials that have similar properties (melting point, malleability, hardness), such as bismuth and tin. Bismuth and tin sinkers can be produced using the molding process that is typically used to produce lead sinkers although different molds may be required. The manufacture of tin split-shot may require greater precision than the manufacture of lead split-shot in order to prevent damage to the fishing line from the hard edges on tin sinkers. Bismuth expands as it solidifies and therefore may require the use of high-quality milled molds. (Scheuhammer, Norris 1995)The lower melting point of bismuth and tin may result in lower energy costs than those for equivalent lead sinker production. Bismuth and tin sinkers can be manufactured by individuals at home using lead sinker molds (USEPA 1994).

Manufacturers switching from lead to steel would be required to make significant investments in capital equipment. The high melting point and hardness of steel make it impractical to manufacture steel sinkers using a molding operation. Steel sinkers can be produced using machining operations. (Ellis) An alternative to investing in steel machining equipment would be to outsource the production of the steel sinkers to a supplier with steel machining capabilities.

Ceramic sinkers are produced in a mold and then fired in a high temperature furnace. A manufacturer of ceramic sinkers, Big Ten Tackle, avoided the investment in production equipment by outsourcing the production of the ceramic components to a company that specializes in the production of ceramic parts.

While tungsten sinkers can be produced using a molding operation, the 6100° F melting point of tungsten eliminates the possibility of switching lead sinker molding equipment to tungsten sinker production. Therefore a switch from lead to tungsten would require significant capital investment unless the tungsten sinkers were produced by a supplier. The high melting point results in high production costs because of the energy costs and the long cooling times (Duke).

Replacement Rate

Fishing sinkers do not typically wear out but are lost during use such as when fishing tackle becomes caught on weeds, rocks or other objects. EPA estimated that 477 million lead, zinc, and brass sinkers are sold each year in the United States for freshwater fishing but it is not clear how many of these sinkers are purchased to replace lost or discarded sinkers.

Key End-of-Product Life Costs

Fishing sinkers are typically lost during use, discarded by anglers in terrestrial habitats or disposed of in household trash. These end-of-life disposal methods bear no cost for the user, manufacturer or retailer. Several state agencies encourage the proper disposal of lead fishing sinkers at municipal household hazardous waste collection events where they would be recycled or disposed of as hazardous waste at a cost to the municipality.

Bismuth, ceramic, steel, tin and tungsten fishing sinkers are not considered to be hazardous and can be disposed of in household trash.

Tables 3.4.3G-K provide additional financial data for each of the alternatives.

Table 3.4.3 G: Fishing Sinkers – Bismuth

	Financial Parameter	Measure/Metric	Source of Information
		Required Data	
	Initial purchase price for chemical/alternative	In 2005, bismuth dealer prices fluctuated from an average of \$3.55/lb in the first quarter to an average of \$4.57/lb in the fourth quarter. The fourth quarter 2005 price represented a 33% increase over the fourth quarter 2004 price.	Carlin, 2006a
		Lead raw material price: \$0.65/lb, Platts Metals Week North American producer price, December 2005	Gabby, 2006a
		A major U.S. fishing sinker manufacturer (Water Gremlin) said that its cost to purchase lead was \$0.30/lb in 2003.	Myers, 2003
	Initial purchase cost for end-product/component	Egg Sinkers: Prices range from \$0.33 for a 1/8 oz sinker to \$1.00 for a 3/4 oz sinker. Prices are approximately 5 to 6 times the price of lead egg sinkers (Cabela's, 2006). Worm Weights: Prices range from \$0.24 for a 1/16 oz weight to \$0.45 for a 1/4 oz weight. Prices are approximately 4 to 6 times the price of lead worm weights (Bass Pro, 2006) (FishUSA, 2006). Note: The bismuth sinkers were typically sold in packages with smaller quantities of sinkers than the equivalent lead sinkers, which may affect a per unit price comparison.	Cabela's, 2006 Bass Pro, 2006 FishUSA, 2006
	Availability of chemical/alternative	All primary bismuth consumed in the U.S. is imported and less than 5% is obtained by recycling old scrap. Belgium was the leading supplier to the U.S., followed by China, Mexico, and the U.K. Bismuth is a byproduct of processing lead ores, and in China, it is a byproduct of tungsten ore processing. Bismuth consumption in the U.S. in 2005 was estimated at 2,280 metric tons. Worldwide demand is growing at about 5% per year, driven in part by its use as a replacement for lead but a global shortage is not expected. Low prices could constrain bismuth supply to the market.	Carlin, 2006a
	Availability of component/end-product	The following types of fishing sinkers are available from major retailers that sell fishing sinkers online: - Egg sinkers - Worm weights Bismuth split shot sinkers were not carried by several major online retailers.	Bass Pro, 2006 Big Ten, 2006 Cabela's, 2006 FishUSA, 2006 Wal-Mart retail store, Bellingham, MA, March 2006.
	Capital costs	Bismuth sinkers may be produced using a molding process that is similar to the process used to produce lead sinkers although different molds may be required. Bismuth expands as it solidifies and therefore may require the use of high-quality milled molds. The lower melting point of bismuth may result in lower energy costs than those for equivalent lead sinker production. Bismuth sinkers can be manufactured by individuals at home using lead sinker molds.	USEPA, 1994 Scheuhammer, 1995

Table 3.4.3 H: Fishing Sinkers – Ceramic

	Financial Parameter	**Measure/Metric**	**Source of Information**
Required Data			
	Initial purchase price for chemical/alternative	According to a manufacturer of ceramic sinkers, ceramic sinkers cost 33% more per pound than lead. Lead raw material price: $0.65/lb, Platts Metals Week North American producer price, December 2005. A major U.S. fishing sinker manufacturer, Water Gremlin, said that its cost to purchase lead was $0.30/lb in 2003.	McMahon, 2006b Gabby, 2006a Myers, 2003
	Initial purchase cost for end-product/component	Slip Sinkers: Prices range from $0.33 for a 1/2 oz sinker purchased in a package of 24 to $0.42 for a 1/2 oz sinker purchased in a package of 12. Prices are approximately 2 to3 times the price of lead slip sinkers. Note: The ceramic sinkers were sold in packages with smaller quantities of sinkers than the equivalent lead sinkers, which may affect a per unit price comparison.	Big Ten, 2006 FishUSA, 2006
	Availability of chemical/alternative	Availability of steatite ceramic would not be affected by increased production of ceramic sinkers. Talc, including steatite, is mined in many countries including the U.S. and is used in a wide variety of products, including paper, talcum powder, paint filler, and ceramic products such as electrical insulators. U.S. mines produced around 1 million metric tons of crude talc ore per year during the 1990's.	USGS, 2000
	Availability of component/end-product	Ceramic sinkers were not available at three major online retailers (Cabela's, Bass Pro Shops & FishUSA.com) or at Wal-Mart stores. An internet search located only one company selling ceramic weights (Big Ten, 2006).	Bass Pro, 2006 Big Ten, 2006 Cabela's, 2006 FishUSA, 2006 Wal-Mart retail store, Bellingham, MA, March 2006.
	Capital costs	Ceramic sinkers are produced in a mold and then fired in a high temperature furnace. This manufacturing process is significantly different than the molding process used to produce lead sinkers and therefore a significant capital investment would be required to switch from lead sinker production to ceramic sinker production. A manufacturer of ceramic sinkers, Big Ten Tackle, avoided the investment in production equipment by outsourcing the production of the ceramic components to a company that specializes in the production of ceramic parts.	McMahon, 2006b

Table 3.4.3 I: Fishing Sinkers – Steel

	Financial Parameter	Measure/Metric	Source of Information
		Required Data	
	Initial purchase price for chemical/alternative	The price for hot rolled steel plate in Dec 2005 was approximately $0.29/lb (steelonthenet, 2006). Lead raw material price: $0.65/lb, Platts Metals Week North American producer price, December 2005. A major U.S. fishing sinker manufacturer, Water Gremlin, said that its cost to purchase lead was $0.30/lb in 2003.	steelonthenet, 2006 Gabby, 2006a Myers, 2003
	Initial purchase cost for end-product/component	Bullet Weights: Prices range from $0.07 for a 1/16 oz weight to $0.19 for a 3/4 oz weight. Prices are approximately 1 to 2 times the price of lead bullet weights. Egg Sinkers: Prices range from $0.12 for a 1/4 oz sinker to $0.37 for a 1 oz sinker. Prices are approximately .7 to 2 times the price of lead egg sinkers. Note: The steel sinkers were typically sold in packages with smaller quantities of sinkers than the equivalent lead sinkers, which may affect a per unit price comparison.	Bass Pro, 2006 Cabela's, 2006
	Availability of chemical/alternative	Global crude steel output in 2005 was 1,129 million metric ton. Increased production of steel fishing sinkers will not affect supply or price of steel.	ISSB, 2006
	Availability of component/end-product	Steel bullet weights and egg sinkers were available at two major online retailers (Cabela's & Bass Pro). A Wal-Mart store did not carry steel sinkers. Steel split shot sinkers were not available at several major retailers (store and online).	Bass Pro, 2006 Cabela's, 2006 FishUSA, 2006 Wal-Mart retail store, Bellingham, MA, March 2006.
	Capital costs	Manufacturers switching from lead to steel would be required to make significant investments in capital equipment. The high melting point and hardness of steel make it impractical to manufacture steel sinkers using a molding operation. Steel sinkers can be produced using machining operations (Ellis, 2006). An alternative to investing in steel machining equipment would be to outsource the production of the steel weights to a supplier with steel machining capabilities.	Ellis, 2006

Table 3.4.3 J: Fishing Sinkers – Tin			
	Financial Parameter	**Measure/Metric**	**Source of Information**
		Required Data	
	Initial purchase price for chemical/alternative	Tin raw material price: The Platts Metals Week average composite price for tin in December 2005 was $4.43/lb, which was 7% higher than the November price and 20% less than the December 2004 price. Lead raw material price: $0.65/lb, Platts Metals Week North American producer price, December 2005. A major U.S. fishing sinker manufacturer, Water Gremlin, said that its cost to purchase lead was $0.30 per pound in 2003. Its cost for tin was $3.00/lb.	Carlin, 2006b Gabby, 2006a Myers, 2003
	Initial purchase cost for end-product/component	Removable Split Shot Sinkers: Prices range from $0.02 for a BB size sinker to $0.19 for a #1 size sinker. Prices are approximately 1.5 to 4 times the price of lead removable split shot sinkers. Note: The tin sinkers were typically sold in packages with smaller quantities of sinkers than the equivalent lead sinkers, which may affect a per unit price comparison.	Bass Pro, 2006 Cabela's, 2006 Wal-Mart retail store, Bellingham, MA, March 2006.
	Availability of chemical/alternative	Tin has not been mined in the United States since 1993. World tin reserves appear to be adequate to meet foreseeable demand. Domestic demand for primary tin is expected to grow slowly in the next few years, at a rate of about 1% per year. That rate, however, could double in a few years if new applications - especially those in which tin is substituted for toxic materials, such as lead-free solders - find acceptance in the marketplace. Recycling: About 9,000 tons of tin from old and new scrap was recycled in 2005. Of this, about 5,000 tons was recovered from old scrap at 2 detinning plants and 91 secondary nonferrous metal processing plants. Import Sources (2001-04): Peru, 44%; China, 14%; Bolivia, 14%; Indonesia, 11%; and other, 17%.	Carlin, 2006b
	Availability of component/end-product	Tin split shot sinkers were available at two major online retailers (Cabela's & Bass Pro) and at Wal-Mart stores. Other types of tin fishing sinkers were not available at these major retailers. However, one company, Warrior Sporting Goods, offers a line of tin sinkers including egg, cannon ball, walking, and split shot sinkers.	Bass Pro, 2006 Cabela's, 2006 FishUSA, 2006 Wal-Mart retail store, Bellingham, MA, March 2006. Warrior, 2006

Table 3.4.3 J: Fishing Sinkers – Tin

	Financial Parameter	**Measure/Metric**	**Source of Information**
	Required Data		
	Capital costs	Tin sinkers can be produced using the molding process that is typically used to produce lead sinkers although the different molds may be required. The manufacture of tin split-shot may require greater precision than the manufacture of lead split-shot in order to prevent damage to the fishing line from the hard edges on tin sinkers. The lower melting point of tin may result in lower energy costs than those for equivalent lead sinker production. Tin sinkers can be manufactured by individuals at home using lead sinker molds (USEPA, 1994) According to a manufacturer of tin weights, Warrior Sporting Goods, tin weights can be manufactured using the same molds used to manufacture lead weights (Myers, 2003).	USEPA, 1994 Myers, 2003

Table 3.4.3 K: Fishing Sinkers – Tungsten

	Financial Parameter	**Measure/Metric**	**Source of Information**
	Required Data		
	Initial purchase price for chemical/alternative	In 2005, tungsten prices fluctuated from approximately $2.72/lb in January to approximately $9.98/lb in May. Lead raw material price: $0.65/lb, Platts Metals Week North American producer price, December 2005. A major U.S. fishing sinker manufacturer, Water Gremlin, said that its cost to purchase lead was $0.30/lb in 2003.	DesLauriers, 2005 Gabby, 2006a Myers, 2003
	Initial purchase cost for end-product/component	Bullet Weights: Prices range from $0.54 for a 1/8 oz weight to $2.15 for a 1 oz weight. Prices are approximately 9 to 12 times the price of lead bullet weights (Bass Pro & Cabela's). Drop Shot Weights: Prices range from $0.75 for a 1/8 oz weight to $3.00 for a 1/2 oz weight. Prices are approximately 3 to 7 times the price of lead drop shot weights (Bass Pro & Cabela's). Worm Weights: Prices range from $0.56 for a 1/8 oz sinker to $2.25 for a 1-1/2 oz sinker. Prices are approximately 7 to 12 times the price of lead worm weights (Bass Pro & FishUSA). Note: The tungsten sinkers were typically sold in packages with smaller quantities of sinkers than the equivalent lead sinkers, which may affect a per unit price comparison.	Bass Pro, 2006 Cabela's, 2006 FishUSA, 2006

Table 3.4.3 K: Fishing Sinkers – Tungsten

	Financial Parameter	Measure/Metric	Source of Information
	Required Data		
	Availability of chemical/alternative	U.S. consumption of tungsten materials in 2005 was 11,600 metric tons (Shedd, 2006). World tungsten supply is dominated by Chinese production and exports. The Chinese government regulates tungsten production and the total volume of tungsten exports, and the Government has gradually shifted the balance of export quotas towards value-added downstream tungsten materials and products. In 2005, inadequate supplies of tungsten concentrates within China combined with increased demand for tungsten materials in China and elsewhere resulted in steep increases in the prices of tungsten concentrates. The sole Canadian tungsten mine restarted operations. Various companies worked towards developing tungsten deposits or reopening inactive tungsten mines in Australia, China, Peru, Russia, the United States, and Vietnam. Recycling: In 2005, the tungsten contained in scrap consumed by processors and end users represented approximately 40% of apparent consumption of tungsten in all forms.	Shedd, 2006
	Availability of component/end-product	Tungsten bullet weights, drop shot weights and worm weights were available at two major online retailers (Cabela's & Bass Pro Shops). A Wal-Mart store did not carry tungsten sinkers. Tungsten split shot sinkers are not available.	Bass Pro, 2006 Cabela's, 2006 FishUSA, 2006 Wal-Mart retail store, Bellingham, MA, March 2006.
	Capital costs	While tungsten sinkers can be produced using a molding operation, the 6100° F melting point of tungsten eliminates the possibility of switching lead sinker molding equipment to tungsten sinker production. Therefore a switch from lead to tungsten would require significant capital investment unless the tungsten weights were produced by a supplier. The high melting results in high production costs because of the energy costs and the long cooling times (Duke, 2006).	Duke, 2006

Environmental Health and Safety

It is estimated that 2,450 metric tons of lead are used each year in the United States to produce approximately 477 million fishing sinkers (USEPA 1994). While the fate of lead fishing sinkers is not known, studies indicate that sinkers are commonly lost during use, either in bodies of water used by anglers or on the shores of these bodies of water. In a study conducted by the University of Arizona, interviews with over 850 anglers revealed that anglers lost, on average, one sinker every six hours of fishing (Duerr, DeStefano 1999). Another survey conducted in 1986 estimated that four to six split-shot sinkers might be spilled and lost for every one used (Lichvar 1994).

Biologists have studied the effects of lead sinkers and jigs on waterbirds, such as loons and swans, since the 1970s. Their ongoing research has documented that, in the northeast United States and Canada where loons breed, lead sinkers or jigs can account for 10 -50% of dead adult loons found by researchers (New Hampshire Fish and Game Department). The U.S. Fish and Wildlife Service identified lead poisoning resulting from the ingestion of lead fishing sinkers as a significant cause of mortality of the Common Loon in the United States and Eastern Canada (Evers, 2004). A study of mortalities of common loons in New England found that the most common cause of death in adult breeding loons was lead toxicity from ingested fishing sinkers) (Pokras, Chafel 1992).

A single fishing sinker swallowed with food or taken up as grit could be fatal to waterbirds. Lead adversely affects the function and structure of the kidney, central nervous system, bones, and production and development of blood cells in waterbirds. Exposure to lead, such as through ingestion of fishing sinkers, can cause lead poisoning in waterbirds, producing convulsions, coma, and death (USEPA 1994).

In a 1994 study, EPA stated that it did not find any information to indicate that bismuth or tungsten are toxic to avian species. Results of a research program on lead-free alternatives to lead shot conducted by the Fish and Wildlife Service indicated that steel and tin are less toxic than lead to ducks when ingested (USEPA 1994).

In the same 1994 study, EPA estimated that 0.8 – 1.6 million anglers in the U.S. produce their own lead sinkers at home. This activity has the potential to expose individuals and family members to airborne lead particles or vapors released during the pouring of molten lead into the fishing sinker molds.

Environmental Assessment

Drinking Water Standards

The National Primary Drinking Water Regulations are legally enforceable standards, set by EPA, that apply to public water systems. In these standards, the Maximum Concentration Level (MCL) for lead in drinking water is 15 μg/L and the Maximum Concentration Level Goal (MCLG) is zero. EPA had not set MCLs for any of the fishing sinker alternatives considered in this assessment.

EPA has also established National Secondary Drinking Water Standards, which are non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water. Steel (iron) is the only alternative fishing sinker material included in this assessment where a secondary standard applies; iron has a secondary standard level of 300 μg/L.

Florida and Minnesota have established maximum concentration levels for tin in drinking water (4200 μg/L and 4000 μg/L respectively).

Affinity for Water: Water Solubility
Lead, bismuth, ceramic, steel, and tin are insoluble in water. It should be noted that certain compounds of these metals may be soluble. Tungsten dissolves in water reaching concentrations up to 475 – 500 mg/L (Strigul, Nicolay, et al. 2005).

Density

Lead has a density of 11.34 g/cm^3, which makes it more dense than all of the alternative materials considered in this assessment, with the exception of tungsten (19.3 g/cm^3). Ceramic (2.6 g/cm^3) is the least dense alternative followed by tin (7.34 g/cm^3), steel (7.87 g/cm^3), and bismuth (9.8 g/cm^3) (Automation Creations).

Bioaccumulation

According to the International Chemical Safety Cards (ICSCs), bioaccumulation of lead may occur in plants and mammals and it is strongly advised that lead does not enter the environment. Specific information on the bioaccumulation of bismuth, ceramic, steel, tin, and tungsten were not available. As discussed earlier in this report, EPA is in the process of developing a framework that will address the issue of bioaccumulation of metals, as well as related issues such as bioavailability.

Aquatic toxicity

National Recommended Water Quality Criteria was used as a source for data on aquatic toxicity of lead and lead-free alternatives. Water Quality Criteria includes the following two aquatic life criteria for both freshwater and saltwater:

- Criteria Maximum Concentration (CMC) – An estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.
- Criteria Continuous Concentration (CCC) – An estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

Lead is listed as a Priority Toxic Pollutant and iron is listed as a Non Priority Pollutant. Bismuth, ceramic, tin and tungsten were not included in the Water Quality Criteria list. **Table 3.4.3 L** shows the Water Quality Criteria for lead and iron.

Table 3.4.3 L: Water quality criteria for lead and iron.

	Freshwater		**Saltwater**	
Priority Pollutant	**CMC (μg/L)**	**CCC (μg/L)**	**CMC (μg/L)**	**CCC (μg/L)**
Lead	65	2.5	210	8.1
Iron	-	1000	-	-

The Water Quality Criteria values indicate that lead is toxic to aquatic organisms, even at relatively low concentrations.

In 1994, EPA addressed the aquatic toxicity of alternatives to lead fishing sinkers in its response to citizens' petition and proposed ban for lead fishing sinkers. In its assessment of aquatic toxicity of lead alternatives, EPA made the following statements about tin: "Tin, in the inorganic form, is generally much less toxic to aquatic organisms (crustaceans and fish) than lead because of its low solubility, poor absorption, low uptake rate, and rapid excretion" (USEPA 1994).

Tungsten was found to have low toxicity to aquatic organisms (crustaceans and algae). EPA stated that it did not find any information to indicate that bismuth or steel are toxic to aquatic species.

Human Health Assessment

Acute Human Effects

Occupational Exposure Limits

IDLH

The Immediately Dangerous to Life or Health Concentrations (IDLH) for lead is 100 mg/m^3. The IDLH for tin is also 100 mg/m^3. Data on the IDLH for bismuth, steel and tungsten were not located. For iron, 1-2 grams may cause death but 2-10 is usually ingested in fatal cases. The steatite ceramic used for fishing sinkers may have 0-3% quartz. The IDLH for quartz (crystalline silica as respirable dust) is 50 mg/m^3. Steatite ceramic may also have magnesium oxide, which has an IDLH of 750 mg/m^3.

PEL

The Permissible Exposure Level (PEL) for lead is 0.050 mg/m^3 (8-hour TWA). The PEL (TWA) for tin is 2 mg/m^3. PELs have not been established for bismuth, steel and tungsten. The steatite ceramic used for fishing sinkers may have 0-3% quartz as a contaminant. The PEL for quartz (crystalline silica as respirable dust) is either 250 million parts per cubic foot (mppcf) divided by the value "%SiO2 + 5" or 10 mg/ m^3 divided by the value "%SiO2 + 2." Steatite ceramic may also have magnesium oxide, which has a PEL of 15 mg/m^3.

REL

The Recommended Exposure Level (REL) for lead is 0.050 mg/m^3 (TWA). The REL (TWA) for steel (iron) is 1 mg/m^3; for tin it is 2 mg/m^3; and for tungsten it is 5 mg/m^3. An REL has not been established for bismuth. The steatite ceramic used for fishing sinkers may contain 0-3% quartz. The REL for quartz (crystalline silica as respirable dust) is 0.05 mg/m^3. Steatite ceramic may also contain magnesium oxide, but an REL has not been established for magnesium oxide.

Irritation

Dermal

Lead and bismuth do not cause dermal irritation. Skin exposure to iron, tin, tungsten and the quartz and magnesium oxide in ceramic may cause dermal irritation.

Ocular

Dust from lead and all of the lead-free alternatives can cause ocular irritation.

Respiratory

Dust from lead was not identified as a respiratory irritant, while bismuth, ceramic, steel (iron), tin and tungsten can cause respiratory irritation.

Chronic Human Effects

Mutagenicity and Carcinogenicity

Lead is classified as both a mutagen and probable human carcinogen (IARC 2B). The lead-free alternatives in this assessment (bismuth, ceramic, steel, tin and tungsten) are not classified as either mutagens or carcinogens. If the ceramic used for fishing sinkers contains quartz, crystalline silica may be present during production. Crystalline silica (respirable size) is a known human carcinogen (IARC 1A).

Reproductive and Developmental Toxicity

Lead has been identified as a developmental toxicant in humans. Children are particularly sensitive to the chronic effects, which include slowed cognitive development and reduced growth. High lead exposure is also associated with reproductive effects, such as decreased sperm count in men, spontaneous abortions in women and low birthweight (USEPA).

The lead-free alternatives in this assessment (bismuth, ceramic, steel, tin and tungsten) have not been identified as reproductive or developmental toxicants.

Assessment Summary

The following table summarizes the alternatives assessment for lead fishing sinkers.

Table 3.4.3 M: Assessment Summary of Alternatives for Lead Fishing Sinkers

Assessment Criteria		Lead (Reference)	Comparison Relative to Lead				
			Bismuth	Ceramic	Steel	Tin	Tungsten
Technical and Performance Criteria	Density	11.34 g/cm^3	-	-	-	-	+
	Hardness (desirable for "feel" and noise)	Soft Mohrs: 1.5	+	+	+	= (pure) + (alloy)	+
	Malleability (split-shot application)	Yes	-	-	-	=	-
	Low Melting Point (for home production)	622 °F	+	-	-	+	-
	Corrosion Resistant	Yes	=	=	-	=	=
Environmental Criteria	Highly toxic to waterfowl	Yes	+	?	+	+	+
	Toxic to Aquatic Species	Yes	+	?	+	+	+
	Primary Drinking Water Standards (MCL Action Level)	15 μg/L	?	?	+ (iron)	+ (FL & MN)	?

Assessment Criteria		Lead (Reference)	Comparison Relative to Lead				
			Bismuth	**Ceramic**	**Steel**	**Tin**	**Tungsten**
Human Health Criteria	Carcinogenicity	EPA B2 IARC 2B	+	+	+	+	+
	Developmental Toxicity	Yes (Prop 65)	+	+	+	+	+
	Occupational Exposure: REL (8-hour TWA)	0.050 mg/m^3	?	+	+	+	+
Cost	Retail Price	Low	-	-	- / = / +	-	-
	Availability of End-product	Excellent	-	-	-	-	-

Comparison Key + Better = Similar - Worse ? Unknown

3.4.4 Alternatives Assessment for Heat Stabilizers for PVC Wire and Cable Coatings

Technical Assessment

Introduction

Lead and non-lead heat stabilizers are used extensively in various PVC wire and cable applications. There are thousands of different PVC formulations commercially available to meet the varying requirements of different wire and cable applications. The U.S. EPA is undertaking a detailed life cycle assessment for three specific wire and cable applications. The U.S. EPA effort will examine various heat stabilizer technologies for these products including lead, calcium/zinc, and barium zinc. The U.S. EPA effort will also examine various alternative resins used in these product types including: polyvinyl chloride (PVC), polyethylene (PE), fluorinated ethylene propylene (FEP), and possibly, high density polyethylene (HDPE), and ethylene vinyl acetate (EVA). Given the U.S. EPA's ongoing efforts in this area, this report will provide an overview of the current state of the use of non-lead heat stabilizers for PVC wire and cable applications, instead of a detailed alternatives assessment for alternative materials. The major elements of this overview will include:

- Materials used in wire and cable applications
- Lead and non-lead chemicals used for heat stabilizers
- Considerations for selecting heat stabilizers: performance requirements, financial impact, environmental and health issues, drivers for change, and synergistic materials
- Introduction of other on-going initiatives addressing heat stabilizer usage

Wire and Cable Materials

Wire and cable applications are increasing with the growing use of computers, the Internet, cable television, and the increase in electrical power service worldwide. Wire and cable constructions range from the simple – such as building wire, to the complex – such as power cable and fiber optics. There are numerous coated wire and cable manufacturers in Massachusetts that have reported under the Toxics Use Reduction Act in Massachusetts. In general, Massachusetts companies in the wire and cable industry provide higher value products for niche applications such as fiber optic, transportation, industrial, and communications. Massachusetts has the largest number of coated wire and cable manufacturers of any U.S. state. With sales of over $800 million and more than 3,400 employees (based on 1997 U.S. Census and 2002 U.S. EPA Toxics Release Inventory data), the industry is an important part of the Commonwealth's industrial manufacturing base.

Each type of wire and cable, has several common elements including the core (typically copper or fiber optic), insulation, and jacketing. The core is a key component that is used to transfer electrical energy or light from point to point. A fiber optic cable transmits a signal using a wave of light, while copper wires transmit a signal using an electric current. Another of the key components of a wire is its insulation. Its selection is determined by a number of factors such as stability and long life, dielectric properties, resistance to high temperature, resistance to moisture, mechanical strength, and flexibility. There is no single insulation that is ideal in every one of these areas. It is necessary to select a cable with the type of insulation, which fully meets the requirements of the application. Jackets cover and protect the enclosed wires or core against damage, chemical attack, fire and other harmful elements that may be present in the operating environment.

There are eight major types of materials used in coated wire and cable.

(1) *resins* (thermoplastic and thermoset compounds) for insulation, jacketing and cross-webs;

(2) *plasticizers* to make the plastic flexible and easy to process (and impart other qualities such as impact resistance and abrasion resistance);

(3) *stabilizers* to provide heat resistance during manufacturing as well as visible light, UV-rays and heat resistance during product use;

(4) *flame retardants* to slow the spread of an accidental fire and reduce the amount of heat and smoke released;

(5) *fillers* to reduce formulation costs and improve insulation resistance;

(6) *lubricants* to improve the ease of processing;

(7) *colorants* to give the desired color, which is crucial for identification purposes; and

(8) *core* includes materials such as copper and aluminum that carry movable charges of electricity, or fiber optic materials that transport light.

Wire and Cable Applications

There are several major types of wire and cable products defined by their end use. The list below describes the major wire and cable applications (Graboski 1998).

- **Building wire** – Used to distribute electrical power to and within residential and non-residential buildings. Products are sold through home center and hardware retail chains, electrical distributors and to industrial customers and OEMs.
- **Telecommunications wire** – Twisted pair conductors that are jacketed with sheathing, waterproofing, foil wraps and metal. Used to connect subscriber premises to the telephone company. Products are sold to telecommunications system operators and through telecommunications distributors.

- **Cords, Cordsets, Appliance Wire, other** – Two or three conductor cable insulated with rubber or plastic with a molded plug on one or both ends to transmit electrical energy to power equipment or electronic devices. Products are distributed through distributors, retailers, and to OEMs.
- **Power Cable** – This is insulated wire and cable used to transmit and distribute electrical energy. Products are generally sold to the public utility sector.
- **Coaxial and antennae cable** – Primary applications of this type of cable are broadcasting, cable television signal distribution and computer networking. Products are sold directly to Community Access Television (CATV) operators and through distributors.
- **Electronic and data wire** – This type represents high-bandwidth twisted pair copper and fiber-optic cable. It is used to wire subscriber premises above ceilings and between floors to interconnect components. Growth has been driven by expansion of local and wide area networks..
- **Magnet Wire** – Typical applications are electronic motors, generators, transformers, televisions, automobiles and small electrical appliances.

Wire and Cable Properties

Wire and cable products are manufactured to meet a set of application specific performance standards. The major performance categories include electrical, thermal, and mechanical properties, and are listed in the table below.

Table 3.4.4 A: Wire and Cable Performance

Property	Unit of Measurement	Test Method
Electrical:		
Volume resistivity	Ohm-cm	ASTM D257
Dielectric constant (at 1, 10 Khz, and 1, 10 Mhz)	Ratio	ASTM D149
Dissipation factor (at 1, 10 Khz, and 1 Mhz)	Ratio	None listed
Thermal:		
Maximum Operating/ Service Temperature	Degrees C, F	UL 1007, UL 1015, UL 1569
Minimum temperature (brittle)	Degrees C, F	D746
Thermal stability	Minutes at 180 degrees C	None listed
Mechanical:		
Tensile strength	MPa	ASTM D412
Specific gravity/density	SG is unitless	ASTM D792
Hardness	Shore durometer scale	ASTM D2240

Table 3.4.4 A: Wire and Cable Performance

Property	Unit of Measurement	Test Method
Elongation at break	Percent elongation	ASTM D412
Fire resistance/ Flame rating	V-O, HB	UL 94
Smoke test (Arapaho)	None listed	ASTM D4100
Smoke index	None listed	NES-711
Flame Test	cm	IEC 332-3C
Mold shrink, linear flow	In/in	ASTM D955
Limiting Oxygen Index	Percentage oxygen	ASTM D2863
Relative Temp Index mechanical	Degrees C, F	UL 746
Relative Temp Index electrical	Degrees C, F	UL 746
Comparative tracking index	Performance Level Categories	UL 746
Sunlight Resistance	None listed	UL 720 hour Sunlight Resistance
Hot wire ignition	Performance Level Categories	UL 746
High amp arc ignition	Performance Level Categories	UL 746
Halogen content	Percent halogen materials	None listed
Acid gas	mg	MIL-C-24643
Acidity of gases	pH	IEC-754-2
Conductivity	uS/cm	IEC-754-2
Toxicity index	None listed	NES-713

Source: Numerous Wire and Cable Manufacturer Data Sheets

This table was provided to illustrate the many diverse performance characteristics that should be considered when evaluating new materials for wire and cable products. However, it is beyond the scope of this study to identify which of these various electrical, thermal, and mechanical properties are most important for each of the many wire and cable applications.

Additional consideration for the selection of materials for the various wire and cable designs is the applicability of national, state, and local codes and standards. Numerous organizations provide wire and cable guidance and requirements such as: American Society for Testing and Materials (ASTM), National Fire Protection Association (NFPA), Insulated Cable Engineers Association (ICEA), National Electrical Manufacturers Institute (NEMA), American National Standards Institute (ANSI), and International Electrotechnical Commission (IEC) (AlphaGary). It is beyond the scope of this study to identify and evaluate the various wire and cable national, state, and local codes and standards.

Polyvinyl Chloride Overview

There are numerous resins that are used for wire and cable applications including: polyvinyl chloride (PVC), polyethylene, chlorinated polyethylene, cross linked polyethylene, nylon, polypropylene, fluorinated ethylene-propylene (FEP), Teflon, thermoplastic rubber, silicone, ethylene propylene rubber (EPR), styrene butadiene rubber, ethylene propylene diene elastomer (EPDM), polyolefin, and polyurethane. These materials have various performance characteristics that are desirable for different applications. This report will focus on the PVC resin because it used in many wire and cable applications and because lead is commonly incorporated as an auxiliary material for heat stabilization. Lead stabilizers may also be used in some rubbers and elastomers, but those uses were not assessed in this study. The following table illustrates the resins used for wire and cable products.

Table 3.4.4 B: Volume of US Thermoplastic Resins in Wire and Cable - 2000

Thermoplastic resin	Million lb.	Percent
Polyethylene and copolymers	578	46%
PVC	486	39%
Nylons	74	6%
Fluoropolymers	50	4%
Polypropylene	16	1%
Other	53	4%
Total	1257	100%

Source: BCC, Inc. 2000 P-133R

PVC is produced by the polymerization of vinyl chloride monomer in liquid form. PVC is a versatile thermoplastic that is compounded with plasticizers, flame retardants, stabilizers, fillers, lubricants, and colorants, and extruded onto the wire or cable. This report focuses on the use of lead as a heat stabilizer in flexible PVC for wire and cable applications.

While no data are available on the amount of lead stabilizers used in PVC for wire and cable, in 2002, approximately 544 million pounds of PVC were consumed in North America for various wire and cable products. In the U.S., the distribution of PVC consumption for wire and cable is shown in the following table.

Table 3.4.4 C U.S. Consumption of PVC Resins in Wire and Cable in 2002
(Linak, Yagi 2003)

Wire and Cable Application	Percentage (based on weight)
Building wire and power cables	40%
Communication and signal wire	20%
Flexible cord (for household lamps and extension cords)	15%
Appliance wire	10%
Automotive electric wire and other automotive uses	5%
Other	10%
Total	100%

The general performance characteristics of PVC include mechanical toughness, weather resistance, water resistance, good electrical insulating properties, and inherent resistance to mildew and ultraviolet light. The major drawbacks to using PVC include the need for plasticizers for flexible applications and its relatively low decomposition temperature of 212 degrees F.

The types of materials used in a wire and cable depend largely on the specific resin system (e.g. thermoset polyethylene versus cross-linked polyethylene versus polyvinyl chloride) and the requirements for a particular application (*i.e.,* plenum rise communications wire versus high voltage power cable). PVC resin alone cannot be used for thermoplastic processing unless various additives are used to meet the various requirements for specific wire and cable applications. Since there is a wide variety of raw materials and there are continual developments in PVC compounding technology, there are thousands of formulations available. (Wire Association) Table 3.4.4D presents the basic materials used in PVC wire and cable coatings. This table outlines typical polyvinyl chloride formulations for different applications.

When reviewing the formulations in this table, note that:

- The formulations are presented in phr (parts per hundred resin) – a common way to present wire and cable formulations. To convert to weight percent, divide individual phr by total number of parts. Multiply this factor by 100 to get weight percent.
- The formulations are designed to meet Underwriter Laboratory (UL) test specifications.
- The formulations are generic and would require adjustments for specific applications.
- Some of the ingredients use trade names

Table 3.4.4 D: Various Polyvinyl Chloride Insulation Compositions (Wickson 1993)

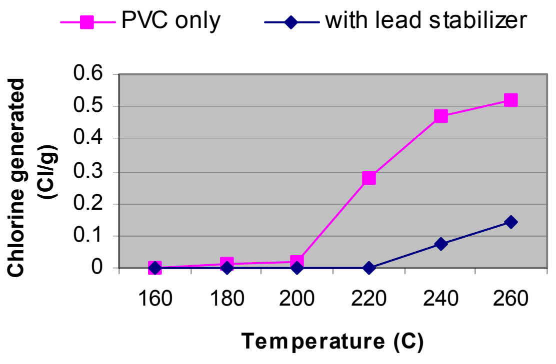
UL Designation	T-TW	THW-THWN	NM-B	THH-THHN	Units
Temperature Rating	**60°C**	**75°C**	**90°C**	**90°C**	**phr**
Polyvinyl Chloride (Resin)	100	100	100	100	phr
DiIsoDecyl Phthalate (Plasticizer)	45	35			phr
Ditridecyl Phthalate (Plasticizer)		15	30	20	phr
Tri Octyl Trimellitate (Plasticizer)			15	35	phr
CaCO3 (Filler)	20	20		15	phr
Clay (Filler)	10	10	7	15	phr
Wax	0.5	0.3	0.5	0.3	phr
Bisphenol A (stabilizer)			0.2	0.3	phr
Sb2O3 (flame retardant)				3	phr
Tribasic lead sulfate (stabilizer)	4	5			phr
Basic lead sulfophthalate (stabilizer)			6	7	phr

Wire and cable extruders purchase either PVC resin to do their own compounding, or purchase the palletized compound.

Heat Stabilizers for PVC Wire and Cable Coatings Overview

PVC resin begins to degrade at temperatures of roughly 160 °C via dehydrochlorination. Since PVC is generally processed at temperatures between 160 °C and 210 °C, stabilizers are necessary to manufacture PVC resin products such as wire and cable. Stabilizers are added to improve heat resistance during manufacturing, and to elevate the resistance of products during use against external impacts such as moisture, visible light, UV-rays and heat. Figure 2 shows the PVC heat degradation relationship between chlorine generation and temperature (Mizuno, et al. 1999).

Figure 2: Heat Degradation of PVC



There are four major categories of primary heat stabilizers used for PVC resins:

- Lead compounds
- Mixed metal salt blends
- Organotin compounds
- Organic compounds

Each of these categories will be described in detail in the next four sections of the report.

Lead compounds

Lead compounds have been the predominant stabilizer in wire and cable worldwide as a result of its cost-effectiveness and excellent electrical insulation properties (*e.g.,* for wet electrical applications). PVC is the only plastic material in which lead is commonly used as a heat stabilizer. Tribasic lead sulfate is thought to be the most widely used PVC stabilizer worldwide. Tribasic lead sulfate is usually used at a level of 4 – 5 parts per hundred resin (phr), although this level may be reduced with optimal resin and plasticizer selection. Tribasic lead sulfate stabilizers are available from several suppliers.

An advantage of lead stabilizers is that the lead chloride produced during the stabilization process does not promote dehydrochlorination. Lead stabilizers also provide excellent wet electrical characteristics for PVC compounds.

There are many different forms of lead compounds that are used as heat stabilizers for various PVC applications. These various lead compounds are listed below (OTA Focus Group June 22, 2004).

- Tribasic lead sulfate CAS 12202-17-4
- Dibasic lead phthalate (Dipthal) CAS 69011-06-9
- Dibasic lead phosphite (Diphos) CAS 1334-40-7
- Tetrabasic lead fumarate CAS 13698-55-0
- Tribasic lead maleate CAS 12275-07-9
- Tetrabasic lead sulfate CAS 52732-72-6
- Monobasic lead sulfate CAS 12036-76-9
- Dibasic lead stearate (co-stabilizer) CAS 12578-12-0
- Normal lead stearate (co-stabilizer) CAS 1072-35-1
- Basic lead carbonate CAS 1319-46-6

Section 3.4 Additional Heat Stabilizer Product Information provides a listing of commercially available lead heat stabilizer products for various wire and cable applications. Information provided in this section includes manufacturer name, model name, chemical(s) used, and key performance attributes.

Mixed Metals

Mixed metals are often used as heat stabilizers in flexible PVC products such as wire and cable. The most common mixed metals used are barium/zinc, calcium/zinc, magnesium/zinc, magnesium/zinc/aluminum, and magnesium/aluminum (hydrotalcite). Barium/cadmium is another mixed metal used as a heat stabilizer, but it has mostly been phased out due to cadmium toxicity concerns. However, it is still commercially available for some applications. Mixed metal stabilizers have extensive use as replacements for lead heat stabilizers in PVC wire and cable applications.

Mixed metal powder stabilizers are mixtures with varying constituents. Powder stabilizers described as lubricating are based on blends of stearates, often barium, calcium or zinc. Moderately lubricating powders are based on laurates rather than stearates. Small amounts of calcium carbonate may be added to aid dispersion, and titanium dioxide may be added for color improvement. Other materials may be added to act as antioxidants and hydrogen chloride (HCl) scavengers. For example, mixed metal heat stabilizers may contain polyols such as pentaerythritol that function as HCl scavengers during processing.

Other important materials in mixed metal stabilizers include zeolite and hydrotalcite. Hydrous zeolite is a complex microporous aluminosilicate that is able to exchange 18 – 20% of its weight for HCl. Hydrotalcite is a platy form of magnesium aluminum hydroxycarbonate. It exchanges carbonate for chloride, thus eliminating carbon dioxide and sequestering HCl (Grossman 2006).

Mixed metal heat stabilizers have been used for years in replacing lead stabilizers in wire insulation and jackets with minimal wet electrical requirements. Initially, barium/zinc stabilizers were used for this application, but it is now common to use calcium/zinc/zeolite or calcium/zinc hyrdrotalcite blends. A standard non-lead formulation for 70 degrees C rated nonmetallic building wire (NM-B) jacket to replace a tribasic lead sulfate stabilizer is illustrated in Table 3.4.4E. This formulation requires approximately the same heat stabilizer loading as a formulation with 4 - 5 phr of tribasic lead sulfate.

Table 3.4.4 E: Formulation for Building Wire (NNM-B) Jacket

Material	Parts per Hundred Resin (PHR)
PVC (electrical grade, medium MW)	100
DIDP (electrical grade)	55 – 60
$CaCO_3$	50
Stearic acid	0.25
Calcium/zinc stabilizer	4 – 5
Epoxidized soybean oil (ESO)	0 - 5

Source: Grossman

NM-B insulation often must meet wet electrical requirements, such as maintaining insulation resistance during 6 months in water at 75 degrees Celsius. For insulation with wet electrical requirements, the calcium/zinc stabilizers should be based on hydrotalcite rather than zeolite. A typical formulation for this application is illustrated in Table 3.4.4F. For wet electrical testing at 90 degrees Celsius, the calcined clay should be silane treated to minimize water pickup, and the plasticizer could be trimellitate (*e.g.,* triisononyl trimellitate, TINTM).

Table 3.4.4 F: Formulation for NM-B Insulation

Material	Parts per Hundred Resin (PHR)
PVC	100
Calcined clay (electrical grade)	10
$CaCO_3$	5 - 10
TINTM plasticizer or equivalent	25
Undecyl dodecyl phthalate (UDP) plasticizer or equivalent	25
Calcium/zinc/hydrotalcite stabilizer	4 - 7

Source: Grossman

Another demanding wire and cable application is the stabilization of PVC jackets for plenum cables and other low smoke flame resistant applications. The challenge is to stabilize the brominated flame retardants as well as the resin, and to counteract the destabilizing activity of various low smoke additives. This requires high stabilizer loading, typically 4 – 6 phr for calcium/zinc/zeolite heat stabilizer. A typical formulation for this application is illustrated in Table 3.4.4G.

Table 3.4.4 G: Formulation for PVC Plenum Cables

Material	Parts per Hundred Resin (PHR)
PVC	100
ATH	60
FR plasticizer	40
Zinc borate	9
AOM	4.5
Antimony oxide	1
Antioxidant	0.2
Stearic acid	0.2
Calcium/zinc/zeolite stabilizer	4 - 6

Source: Grossman

The following table indicates the difficulty and cost for transitioning from lead to non-lead heat stabilizers for various wire and cable applications.

Table 3.4.4 H: Lead to Non-Lead Heat Stabilizer Transition (Source: AlphaGary)

Style	Description	Transition	Cost Effect
SPT – 1, 2, 3	Appliances	Fairly easy	Low
TW, THW	Building wire, outdoor flexible cords	Very difficult	Moderate
THHN, THWN	Industrial/residential building wire	Very difficult	Moderate
ST, SJT	300/600 volt flexible cords	Fairly easy	Low
STW, SJTW	300/600 volt flexible cords (outdoor)	Very difficult	Low
CM, CMR	Communications: tray/riser	More difficult	Low
CMP	Communications: plenum	More difficult	Moderate
UL 758	Fixed appliance wire	Difficult	Moderate
Vinyl TPE	Booster, audio	Difficult	Moderate
SEO, SJEO	Service entrance	Fairly easy	Moderate

Organotin compounds

Organotin chemicals are compounds that contain at least one bond between tin and carbon. The organotins are classified by their alkyl groups (octyl, butyl, and methyl) and their ligands such as thioglycolic acid esters, reverse esters, and carboxylic acids. The major applications for organotins include PVC heat stabilizers, catalysts, glass coatings, biocides, and agrichemicals (Batt). Organotin compounds are used primarily for rigid PVC applications such as pressure pipe, drain/waste/vent pipe, siding, profile extrusion, sheets, roofing, and bottles. Sulfur-containing organotin compounds are currently the most efficient and most universally used heat stabilizer among all organotins. For example, organotin mercaptides are able to react with hydrogen chloride and also help impede autoxidation. The combination of these two functions gives the organotin mercaptides excellent thermostabilizing properties.

Organotins can function as heat stabilizers with levels as low as 0.3 phr. Organotins are used for some flexible PVC applications as well such as flooring topcoats and foamed plastisols. However, organotin heat stabilizers have not yet been commercialized as a replacement for lead in PVC wire and cable applications.

Organic compounds

Organic compounds are a new entry in the market and the subject of intense development by the major heat stabilizer producers. Several types are being evaluated including thiol esters and heterocyclic compounds. In the 1980's, Ciba developed a new class of nonmetallic stabilizers based on the carbon nitrogen six membered ring heterocycle 1,2-dimethyl-4-aminouracil. Research has been conducted for aromatic and aliphatic organic thiol compounds to stabilize PVC compositions. Recently, Professor W.H. Starnes from the College of William and Mary has reported that thiol esters such as 2-ethylhexyl 3-mercaptobenzoate function as efficient stabilizers. Although their usage is still very low, they could become a significant factor in the market in response to the pressures to replace heavy metal heat stabilizers. There is a significant research and development effort underway to develop organic stabilizers as an alternative to mixed metal types (Grossman 2006).

It has been reported that the addition of epoxidized soybean oil (ESO) increases the heat stabilizer effectiveness for the thiol esters mentioned above. This includes enhanced performance for dynamic heat stability and decomposition time. Generally, epoxidized soybean oil is utilized in PVC as a hydrogen chloride (HCl) scavenger. Epoxidized soybean oil can be used at a loading of 3 to 10 parts per hundred resin (phr). (Starnes, William Herbert Jr., Du 2004)

Drivers for Change

There are numerous factors that drive companies in the wire and cable industry to switch to less hazardous materials in their products. These factors can be categorized as regulatory and market drivers. For regulatory drivers, the European Union has enacted several directives over the past several years aimed at restricting the use of certain hazardous materials in vehicles and electrical and electronic equipment. In January 2003, The European Union (EU) published directives on Waste Electrical and Electronic Equipment (WEEE) and the Restriction of the use of certain Hazardous Substances in electrical and electronic equipment (RoHS).

The WEEE directive deals with end-of-life management of electrical and electronic equipment (*e.g.,* take-back and recycling of used computers and equipment), whereas the RoHS directive addresses the types of materials that are used in manufacturing electrical and electronic equipment.

RoHS restricts the following six chemicals above certain threshold amounts, with certain exceptions: lead, cadmium, hexavalent chromium, mercury, poly-brominated biphenyls and poly-brominated diphenyl ethers, with an implementation date of July 1, 2006. Companies and suppliers to companies that sell products in the European Union must find safer alternatives for these substances to continue selling into the European marketplace. The regulations also promote re-use and recovery of products, and minimizing the risks associated with recycling and disposing of these products at the end of their useful life.

Japan has its own regulations requiring the recycling of certain electronic products and China has passed a set of its own regulations similar to those of the European Union, with an effective date of March, 2007. In the U.S., drivers include a focus on lead in wire and cable products under California Proposition 65 and the US EPA`s focus on persistent, bioaccumulative and toxic (PBT) substances.

Even in the absence of regulatory requirements, many large companies have taken the initiative to eliminate materials of concern from their products where possible. They are trying to make more environmentally friendly and recyclable products, as well as trying to phase out materials that they believe may be restricted in the future. In particular, many U.S. automotive and electronics companies such as GM, Toyota, Dell and Apple have begun to phase out lead and some halogenated compounds from their products. These requirements move down the supply chain to manufacturers all over the world, who must be able to supply components without these materials or risk loss of business.

Lead and Non-lead Heat Stabilizers for PVC Wire and Cable Coatings: Performance Considerations

The performance of any heat stabilizer depends on the specific application and the formulation used. In general, it was found that the lead-free heat stabilizers can achieve comparable performance properties to the lead heat stabilizers for many applications. The results of some recent performance testing conducted by industry between lead and non-lead heat stabilizers is included to illustrate this point.

Amfine Chemical Corporation is a provider of mixed metal heat stabilizers for use in PVC wire and cable applications. In 2003, Amfine conducted a performance study comparing various electrical and mechanical properties for the following five different PVC formulations.

A: Dibasic lead phthalate and stearic acid
B: Tribasic lead sulphate and dibasic lead stearate
C: Amfine RUP-110GP (Magnesium zinc heat stabilizer)
D: Amfine RUP-110GP (Magnesium zinc heat stabilizer)
E: Amfine RUP-144RT (Magnesium zinc heat stabilizer)

The base formulation for this test is listed in the table below.

Table 3.4.4 I: Base Formulation

Material	PHR
Polyvinyl chloride (PVC)	100
TINTM	25
Diundecyl phthalate (DUP) plasticizer	25
Clay #33	12
Sb_2O_3	4

The results from this performance test are shown in Table 3.4.4 J.

Table 3.4.4 J: Lead and Non-lead Heat Stabilizer Performance Comparison

Material/Performance Property	A	B	C	D	E
Dibasic lead phthalate (phr)	6.0				
Stearic acid (phr)	0.2				
Tribasic lead sulfate (phr)		5.0			
Dibasic lead stearate (phr)		1.0			
RUP-110GP (phr)			6.0	8.0	
RUP-144RT (phr)					6.0
Press plaque, 190 Cx5min (YI)	31.0	24.1	31.5	30.7	29.2
190 Cx30min (YI)	43.7	30.7	36.0	34.1	33.5
Color rating after heat aging 190^0Cx60min (1 for good, 10 for poor)	7.5	7	6.5	6.5	6
Decomposition time at 200 C (min)	90	120~	120	120<	120<
Volume Resistivity (VR) VRx10^{14} Original (Ohm-cm)	0.7	3.8	4.0	3.9	0.9
Immersion Into hot water (90 C)					
VRx10^{14} after 1 week	0.1	0.1	12.7	12.8	16.4
VRx10^{14} after 2 weeks	0.08	0.2	20.8	14.9	23.5
VRx10^{14} after 3 weeks	0.9	2.9	16.1	17.0	39.0
VRx10^{14} after 4 weeks	0.6	0.8	12.8	15..9	22.9
VRx10^{14} after 5 weeks	0.7	1.6	15.4	14.6	16.0
VRx10^{14} after 6 weeks	0.4	4.3	12.1	16.6	12.3
VRx10^{14} after 12 weeks	0.6	2.9	11.3	22.4	10.8
VRx10^{14} after 18 weeks	0.4	3.2	12.4	15.4	15.5
VRx10^{14} after 26 weeks	0.5	2.2	11.5	15.5	14.5
Elongation %	323	336	329	324	324
Tensile strength MPa	31.6	32.0	31.1	30.0	31.6
100% Modulus MPa	19.2	18.6	18.2	18.1	18.6
Weight Loss %	6.0	5.8	5.6	6.3	6.6
Elongation %	271	275	280	265	285
Elongation retention %	84	82	85	82	88
Tensile strength MPa	32.1	32.8	32.5	31.7	33.5
100% Modulus MPa	25.1	25.4	24.8	24.8	24.6

Source: Amfine Datasheet for RUP 144RT

For this testing, the non-lead heat stabilizers had similar or better performance compared to the lead heat stabilizers for mechanical properties such as elongation and tensile strength, and electrical properties such as volume resistivity.

In 2002, Sumitomo Electric Industries published a paper that compared the performance between lead and lead-free heat stabilizers for PVC wire. The lead-free heat stabilizer used for the performance test was a combination of calcium/zinc and hydrotalcite. The outer diameter of the conductor was 0.48 mm, and the thickness of the insulation was 0.5 mm. The results of the performance test are shown in the table below.

Table 3.4.4 K: Lead versus Lead-free Heat Stabilizer Performance Test

Performance Characteristic	Lead-free Stabilizer	Lead Stabilizer
Tensile Strength	19.9 MPa	22.1 MPa
Elongation	117%	109%
Heat Deformation (121 degrees C, 250 g)	60.9	72.8
Flammability (VW-1)	Pass	Pass
Cold Bend (-10 degrees C 1 hour)	No crack	No crack
Volume resistivity (ohms cm)	1.0×10^{14}	2.0×10^{14}

Source: Moriuchi et al.

For this testing, the non-lead heat stabilizers had similar performance compared to the lead heat stabilizers for mechanical properties such as elongation, heat deformation, and tensile strength, as well as electrical properties such as volume resistivity.

Ferro Polymer Additives Division has conducted performance testing to compare their Therm-Chek 7700 heat stabilizer versus a tribasic lead sulfate heat stabilizer. Therm-Chek 7700 is a mixed metal heat stabilizer using aluminum/magnesium/zinc. The testing was done to compare the water absorption and the residual heat stability between the two stabilizer types. The residual heat stability is measured using the Congo Red Test. For this test, the sample is cut into small pieces and then heated. Hydrogen chloride (HCl) released from the sample causes a color change of moist Congo Red. The time duration is measured from the time heat is applied to the sample until the color change occurs. The base formulation for this test is shown in Table 3.4.4L.

Table 3.4.4 L: Base Formulation

Material	Concentration (phr)
PVC	100
DIDP	50
$CaCO_3$	50
Calcinated clay	10
Stabilizer	4

The test conditions were conducted on a 70 g sample weight. The following table indicates the results of the testing.

Table 3.4.4 M: Testing Results

Performance Property	Tribasic Lead Sulfate	Therm-Chek 7700P
Congo Red (200 degrees C)	122	134
Water Absorption (14 days at 70 degrees C)	1.0 %	1.1 %

Source: Ferro, Polymer Additives Division, Therm-Chek 7700P, Technical Datasheet

For this test, the mixed metal stabilizer outperformed the lead stabilizer in the Congo Red test and had comparable water absorption levels with the lead stabilizer.

Synergistic materials

The performance of existing non-lead heat stabilizers may be enhanced through the addition of certain synergistic materials in the PVC resin. Research is underway at the University of Massachusetts Lowell to enhance the performance and practical utility of non-lead heat stabilizers through the addition of a small amount of organically modified clay, to form a layered silicate nano-composite. The objective of this research is to improve the thermal stability, flame retardance, and overall performance of the formulation using the same loadings of commercially available non-lead heat stabilizers. The intent is to take advantage of an effect already demonstrated commercially by nano-composite barrier resins. The dispersed clay platelets improve barrier properties thanks to their high aspect ratio and impermeability, which forces diffusing species to take a highly tortuous path in order to pass through the material.

The addition of clays to such a resin system allows for a number of specific enhancements with respect to what non-lead heat stabilizers already accomplish. First, dispersed clays can increase HCl scavenging efficiency. Second, the cationic surfactants that are ion-exchanged into the inter-layer galleries of the clays can help with dispersing the clay in the polymer (their primary function), but also serving as antioxidants themselves, through inclusion of unsaturated functionalities for instance, further enhancing the thermal stability of these materials. Finally, in addition to the enhanced thermal stability often seen in polymer / clay nanocomposites in general, an additional advantage often seen in these systems is their inherent flame retardance, due to formation of silicate char once burning begins at an exposed surface (Schmidt 2005).

The results reported in United States Patent Number 6872854 indicates that synergistic materials may be used to address the discoloration of the PVC compound when using non-lead heat stabilizers, particularly discoloration in the initial stage of heating. Complexes of metal salts of organic acids in combination with β-diketone compounds, such as calcium benzoate 1,3-diphenylpropane-1,3-dionate (CBDBM), are efficient solid intermediates for halogenated resin stabilizers. When used jointly with other low toxicity intermediates, such as zinc or magnesium intermediates, these stabilizer complexes can replace previously used mixed metal stabilizers containing cadmium, lead and/or other heavy metal compounds (Krainer, et al. 2005).

Financial Assessment

The three major financial impact categories to consider for switching to non-lead heat stabilizer for PVC wire and cable applications are: raw material costs, processing costs, and research/testing/approval costs. The raw material costs are a function of the heat stabilizer raw material price per pound, and the heat stabilizer loading requirements in the PVC formulation. It is challenging to obtain a direct cost comparison between lead and non-lead heat stabilizers. The heat stabilizer prices are typically not published, and actual pricing is negotiated between heat stabilizer vendor and compounder. Further, the heat stabilizer is comprised of numerous constituent materials which may be varied depending on application requirements. Also, PVC heat stabilizers are usually delivered as so-called one packs, which not only contain the heat stabilizers but also lubricants and acrylic processing aids.

Historically, there was a significant price differential between the lead and non-lead heat stabilizers. The premium required for non-lead heat stabilizer was approximately 10 percent approximately four years ago. However, over the past few years the sales volumes of mixed metal heat stabilizers have significantly increased because of greater market acceptance. Consequently, the cost for mixed metal heat stabilizers has decreased. Based upon conversations with heat stabilizer suppliers and compounders, the cost differential between lead and mixed metal heat stabilizers is estimated to now be between cost neutral and a 10% premium for mixed metal heat stabilizers.

The loading requirements for lead and non-lead stabilizers vary depending on the application. In general, the loading requirements between lead and non-lead heat stabilizers are considered to be not significantly different.

From a processing cost standpoint, no new capital equipment is typically required for compounders or wire and cable manufacturers that are transitioning from lead to non-lead heat stabilizers. However, some engineering time is required to make the necessary changes to their process operating profiles.

A significant barrier to switching to new PVC formulations without lead heat stabilizers is the testing and approval costs. Cable manufacturers that change their PVC formulations to eliminate the use of lead as a heat stabilizer must undergo a testing and approval process similar to that required for most formulation changes. Typically, new compounds are initially screened in small scale performance tests to evaluate various mechanical, electrical, thermal, and fire resistance properties. Next, the wire and cable products using the new formulation must be manufactured and evaluated in their finished geometry at third party verification laboratories. The major verification laboratories are Underwriters Laboratories (UL) and ETL Semko. The extent of testing required depends largely on the potential effect the change will have on the critical parameters of the insulation and jacket. It is necessary to check with the testing authority to determine the exact testing required for a given formulation change.

There are up-front research and development efforts required to develop a lead-free substitute for existing compounds using lead stabilizers. This effort has been estimated at approximately 100 man-hours for each new formulation. The testing and approval costs for wire and cable manufacturers are typically between $3,000 to $10,000 per compound per cable. The low end of this range is usually for applications with minimal testing requirements such as a PVC jacket. The high end of this range is typically for applications that require more comprehensive testing such as PVC insulation (AlphaGary Corporation 2002). It may be possible to reduce overall testing costs by obtaining testing and approval for a family of cables at one time, rather than taking a cable by cable approach (Massachusetts Office of Technical Assistance). The following table provides general testing requirements for different applications:

Table 3.4.4 N: Testing Requirements for Various Wire and Cable Applications (OTA)

Application Type	Testing and Approval
Wet-rated wire insulation – *e.g.,* THWN	Standard for Thermoplastic Insulated Wires and Cables – UL 83. The water immersion test at rated temperature takes a minimum of 12 weeks and frequently is completed in 24 weeks.
Power Limited Tray Cable (PLTC)	Cable Tray Flame Test (UL 1685) required and physical testing on samples of the cable jacket, un-aged and after aging in an air oven (typically a seven-day test).
Riser-rated communications cable	Riser Cable Flame Test (UL 1666) and physical testing similar to PLTC cable.
Plenum jacket	NFPA 262 Smoke and Flame Test required. Because of the difficulty in predicting outcomes of this test based on small changes in construction, more testing than for PLTC and CMR constructions may be required.
Flexible Cable –e.g. STP cord	No testing required a priori. Manufacturer responsible for providing assurance that the product meets the UL standard. UL will confirm that the product meets the standard during follow-up testing.
Generically authorized compounds	Substitutions are the responsibility of the cable manufacturer and need not be pre-authorized. UL will confirm that the product meets the standard during follow-up testing.

Environmental, Health, and Safety Assessment

Various lead compounds are used for lead heat stabilizers. Lead compounds have different physical characteristics and chemical properties than lead. Consequently, the environmental and health effects for lead compounds are different than lead. For this study, ten different lead compounds were identified for use in lead heat stabilizers. The most widely used lead compound in lead heat stabilizers is tribasic lead sulfate. The CAS number for tribasic lead sulfate is 12202-17-4, and the chemical formula is $Pb_4O_3(SO_4)H_2O$. Tribasic lead sulfate is comprised of 88 – 90% lead. (Polytrans S.A.) Since there is limited environmental and health data available for tribasic lead sulfate and it is primarily comprised of lead, the environmental, health, and safety properties of lead were used for comparison with lead-free stabilizer alternatives.

The mixed metal heat stabilizer alternatives typically are each comprised of several different chemical compounds. Given the time and resource constraints for this project, the environmental, health, and safety data were collected and reported for five representative mixed metal heat stabilizers. These five heat stabilizers and their constituent chemical compounds are shown in Table 3.4.4 O.

Table 3.4.4 O: Mixed Metal Heat Stabilizers for PVC Wire and Cable Coatings

Manufacturer	Product Name	Chemical Compounds
Amfine Chemical Corp. (Mitsubishi, Asahi Denka)	RUP-103	Magnesium-zinc: Inorganic compounds trade secret (< 80%) Zinc stearate (< 20%) Calcium silicate (< 10%)
Chemtura	Mark EZ 760	Magnesium/aluminum/zinc: Isopropylidenediphenol (< 20%) zinc stearate (< 15%) magnesium aluminum hydroxide carbonate CAS 11097-59-9 (? %)
Chemtura	Mark 6750	Calcium/barium/zinc: Calcium hydroxide (45 – 55%) Barium stearate (20 – 30%) Zinc stearate (10 – 20%) Titanium dioxide (5 – 10%) Trade secret (? %)
Kyowa (Kisuma)	Alcamizer P93	Magnesium/aluminum/zinc: Magnesium zinc aluminum hydroxide carbonate hydrate, CAS 169314-88-9, (95 - 100%) MgO/Al_2O_3 Molar ratio: 3 ZnO/Al_2O_3 Molar ratio: 1
Akrochem Corporation	Zeocros P-321	Magnesium/aluminum: Magnesium aluminum hydroxide carbonate CAS 11097-59-9 (95%) Water (5%)

Sources: (Amfine Chemical Corporation RUP-103 MSDS, 1999, Chemtura Mark 6750 MSDS, 2005, Chemtura Mark EZ 760 MSDS, 2006, Kisuma Alcamizer P93 MSDS, 2005, Akrochem Corporation Zeocros P-321 MSDS, 2005)

In general, the mixed metal alternatives are comprised of chemical compounds that are insoluble or negligibly soluble in water. Consequently, aquatic toxicity for many of these compounds were not identified because of the low water solubility.

From an environmental standpoint, all of the chemical compounds are not considered to be ozone depleting or greenhouse gases. Also, there was no evidence found for these chemicals to be bioaccumulative.

For acute health effects, the following chemicals are considered dermal, ocular, and respiratory irritants: zinc stearate, titanium dioxide, calcium silicate, calcium hydroxide, and isopropylidenephenol. Magnesium zinc aluminum hydroxide carbonate hydrate is considered to be an irritant for dermal and respiratory only. There is no evidence that barium stearate and magnesium aluminum hydroxide carbonate are irritants.

The OSHA-PEL for nuisance dust of 15 mg/m^3 total dust and 5 mg/m^3 for respirable dust is recommended for calcium hydroxide, zinc stearate, calcium silicate, and magnesium aluminum hydroxide carbonate. The oral LD50 (lethal dose) concentrations for rats is shown in the table below for each of the chemicals.

Table 3.4.4 P: LD50 for Various Heat Stabilizer Chemicals

Chemical	LD50 Oral Dose for Rats (mg/kg)
Tribasic lead sulfate	> 2,000
Magnesium aluminum hydroxide carbonate	> 2,000
Isopropylidenephenol	3,250
Barium stearate	3,390
Calcium silicate	3,400 – 5,000
Magnesium zinc aluminum hydroxide carbonate hydrate	> 5,000
Zinc stearate	> 5,000
Calcium hydroxide	7,340
Titanium dioxide	12,000 – 20,000

For chronic health effects, there is no evidence that any of these chemicals cause mutagenicity, reproductive harm, or developmental harm. Except for titanium dioxide, carcinogenicity is not considered an issue for these chemicals. Titanium dioxide is considered by NIOSH to be a potential occupational carcinogen (NIOSH). Also, skin sensitization is not considered an issue for these chemicals with the exception of isopropylidenephenol where skin sensitization is considered possible with repeated exposures.

Significant environmental, health, and safety considerations not previously mentioned in this report for the specific chemicals used in mixed metal stabilizers are listed below.

Zinc stearate: Grossly excessive and chronic inhalation of the dust may cause a progressive chemical pneumonitis, cyanosis, and pulmonary edema. Fine dust dispersed in air in sufficient concentrations, and in the presence of an ignition source is a potential dust explosion hazard (Baker 2004). Thermal oxidative decomposition of this chemical can produce carbon dioxide, carbon monoxide, and zinc oxide fumes.

Calcium silicate: Exposure to this chemical can occur through inhalation, ingestion, or skin contact. No further significant environmental, health, and safety considerations were identified for this chemical.

Isopropylidenephenol: Inhalation and dermal absorption are considered to be major routes of exposure for this chemical. Degradation products for this chemical include carbon dioxide and monoxide.

Magnesium aluminum hydroxide carbonate: Thermal decomposition occurs for this chemical at temperatures greater than 300 degrees Celsius, and acids with $pH < 1$ should be avoided (Kisuma Chemicals BV 2004).

Calcium hydroxide: Dermal absorption is considered possible for this chemical. Calcium hydroxide can have violent reactions with maleic anhydride, mitroethane, nitromethane, nitroparaffins, nitropropane, and phosphorus. Calcium hydroxide is a gastric irritant, and ingestion may be followed by severe pain, vomiting, diarrhea, and collapse. Calcium hydroxide is corrosive and may cause severe burns and blistering upon dermal contact. For ocular contact, it may induce corneal epithelium and blindness (Baker 2005). This chemical decomposes upon heating to produce calcium oxide.

Barium stearate: The decomposition products for this chemical are oxides of barium and carbon. There are limited environmental and health data available for this chemical.

Titanium dioxide: Long term exposure to titanium dioxide dust may result in mild lung fibrosis. Violent or incandescent reactions may also occur with lithium or other pure metals such as aluminum, magnesium, potassium, sodium, and zinc. (Baker 2003)

Magnesium zinc aluminum hydroxide carbonate hydrate: This chemical may be harmful to aquatic organisms due to the presence of zinc, and may cause long-term adverse effects in the aquatic environment. (Kisuma Chemicals BV 2005)

Other Relevant Wire and Cable Initiatives

U.S. Environmental Protection Agency Design for Environment Project

The U.S. Environmental Protection Agency's (EPA) Design for the Environment (DfE) Program and the Massachusetts Toxics Use Reduction Institute (TURI) have formed a partnership with wire and cable industry stakeholders to conduct a life-cycle assessment (LCA) of the insulation and jacketing used in three different wire and cable products. Project partners include wire and cable manufacturers, compounders (i.e. AlphaGary), additive suppliers (i.e. Albemarle), trade association members, TURI, EPA, and project researchers.

The specific goal of the partnership is to evaluate the environmental impacts of the current standard material formulation and alternative formulations for heat stabilizers, flame retardants, and polymer systems for selected wire and cable products, in order to help companies make environmentally sound product and material choices.

The focus of this project will be on the following three product types:

- Category 6, riser-rated communication cable (CMR)
- Category 6, plenum-rated communication cable (CMP)
- Non-metallic sheathed cable, as used in building wire (NM-B)

These products were chosen by the project partners because together they contain materials common to many wire and cable applications, they typically contain materials for which alternatives are being sought, and they represent a significant share of the wire and cable market. The U.S. EPA effort will examine various heat stabilizer technologies for these products including lead, calcium/zinc, and barium zinc. This project will also examine various resins for these product types including: polyvinyl chloride (PVC), polyethylene (PE), high density polyethylene (HDPE), and ethylene vinyl acetate (EVA).

Using a life-cycle assessment approach, the study will generate data to help manufacturers, users, and suppliers of wire and cable incorporate environmental considerations into their decision-making processes. An LCA examines all of the steps involved in manufacturing, using, and disposing of a product or material, and estimates the environmental impacts from each of the following stages: raw material extraction/processing, manufacture, product use/maintenance, and end-of-life disposition. (USEPA 2006)

Massachusetts Toxics Use Reduction Institute: Wire and Cable Supply Chain Program

In 2001, the Massachusetts Toxics Use Reduction Institute (TURI) initiated a multi-year effort to work with the Wire and Cable industry supply chain. This was in response to emerging regulations and market pressures that will affect the hazardous materials used by the industry, including lead compounds, decabromodiphenyl ether, cadmium, and hexavalent chromium. Making successful, robust changes in a product's basic materials requires participation of all parts of the product supply chain, including raw material suppliers, compounders, extruders, and original equipment manufacturers. The Institute's objective is to find alternative safer materials to help the industry remain competitive.

This supply chain program benefits from university research on the environmental impact of wire and cable constituents, laboratory evaluation of alternative materials, and meetings that draw companies from throughout the supply chain together to discuss human and environmental impacts, regulatory requirements, new technology developments, and business and technical strategy.

The Institute has provided several workshops over the past five years. Over 100 professionals from over 6o firms have attended semiannual workshops that span the supply chain, topics covered include updates on the latest regulatory changes, speakers from original equipment manufacturers (OEMs) such as Dell, Microsoft and Xerox, and reviews of innovative products and raw materials such as low-smoke halogen free wiring (Judd Wire, Inc.), heavy metal free jacket and insulation materials (AlphaGary), and lead-free heat stabilizers that pass wet electrical requirements (Teknor Apex).

Vinyl 2010

Vinyl 2010 is a voluntary commitment of the European PVC industry to meet the challenge of sustainable development by undertaking important principles and actions to address PVC manufacture, additives, and waste management. The PVC industry is represented by the following European associations: European Council of Vinyl Manufacturers, European Council for Plasticizers and Intermediates, European Stabilizers Producers Association, and European Plastics Converters. Based on 2000 consumption levels, this voluntary commitment includes a plan to reduce the use of lead heat stabilizers by 50% by 2010, and a 100% reduction by 2015. (European Council of Vinyl Manufacturers (ECVM) et al. 2001)

Massachusetts Office of Technical Assistance (OTA) Greener Cable Initiative

The Office of Technical Assistance for Toxics Use Reduction (OTA) is a non-regulatory office within the Executive Office of Environmental Affairs that helps manufacturers and other toxic chemical users reduce or eliminate their use of toxics and generation of hazardous byproducts. In June 2004, OTA conducted a focus group meeting with the wire and cable industry and has subsequently developed a fact sheet titled, "Strategies for Streamlining Testing and Certification: Environmentally Friendly Wire and Cable". The purpose of this fact sheet is to review strategies for streamlining the testing and certification process, thereby facilitating companies adoption of alternative heat stabilizers and other substances. This initiative has included many companies throughout the supply chain including Halstab, AlphaGary, and Polymer Concentrates.

Additional Heat Stabilizer Product Information

The following tables provide information for the various lead and non-lead heat stabilizers that are commercially available.

Table 3.4.4 Q: List of Alternatives for Lead Heat Stabilizers

Manufacturer	Data Source	Model	Chemical (s)	Performance
Addenda	Datasheet	addiStab - TLF	Tetrabasic lead fumarate (CAS 13698-55-0)	Heat stabilizer used for PVC plenum cable jackets and flexible PVC wire insulation. Used with most sensitive plasticizers, and frequently used with dibasic lead phthalate.
Addenda	Data sheet	addiLube - DBLS	Dibasic lead stearate (CAS 12578-12-0)	Co-stabilizer and lubricant for wire insulation and jacketing. Commonly used in conjunction with lead based heat stabilizers. Typical use level is 0.5 to 1.0 PHR.
Addenda	Data sheet	addiStab-TLM	Tribasic lead maleate (CAS 12275-07-9)	Heat stabilizer for wire insulation and jacketing. Used where photosensitivity is not an issue. Frequently used in combination with dibasic lead phthalate.
Addenda	Datasheet	addiThal	Dibasic lead phthalate (CAS 69011-06-9)	Primary heat stabilizer for flexible PVC. Used for high temperature wire insulation and jacketing.
Addenda	Datasheet	addiBase	Tribasic lead sulfate (CAS 12202-17-4)	Primary heat stabilizer for flexible PVC. Used for low and high temperature wire insulation and jacketing.
Addenda	Datasheet	addiBase-Mono	Monobasic lead sulfate (CAS 12036-76-9)	Primary heat stabilizer for flexible PVC. Used for wire insulation and jacketing. Less reactive with plasticizers than tribasic lead sulfate.

Table 3.4.4 Q: List of Alternatives for Lead Heat Stabilizers				
Manufacturer	**Data Source**	**Model**	**Chemical (s)**	**Performance**
Addenda	Datasheet	addiBase-Tetra	Tetrabasic lead sulfate (CAS 52732-72-6)	Primary heat stabilizer for flexible PVC. Used for low temperature wire insulation and jacketing. Used where photosensitivity is not an issue.
Associated Additives		Almstab	Dibasic lead phosphite	
Associated Additives		Almstab	Normal lead stearate (CAS 1072-35-1)	Secondary stabilizer and lubricant
Associated Additives		Almstab	Basic lead carbonate	Can be used as a PVC stabilizer where the processing temperature does not exceed 180 degrees C.

Table 3.4.4 R: List of Mixed Metal Heat Stabilizers:				
Manufacturer	**Data Source**	**Model**	**Chemical (s)**	**Performance**
Akrochem Corp.	Bill Allen Datasheet MSDS	Zeocros P-321	Magnesium aluminum hydroxy carbonate (95%) CAS 11097-59-9 water (<5%) CAS 7732-18-5	Can be used for wire and cable applications, however, not as effective as lead for water resistance. Has the added benefit of releasing water at 300 degrees Celsius and therefore can be used as a flame retardant.
Akcros (part of Akzo Nobel)		Akcrostab BZ-5043, Lankromark LZB 248	Barium-zinc:	
Amfine Chemical Corp. (Mitsubishi, Asahi Denka)	Jay Kolaya Website Datasheet MSDS	RUP-103	Magnesium-zinc: Inorganic compounds trade secret (< 80%) Zinc stearate (< 20%) Calcium cilicate (< 10%)	For automobile PVC wire harness insulation.

Table 3.4.4 R: List of Mixed Metal Heat Stabilizers:

Manufacturer	Data Source	Model	Chemical (s)	Performance
Amfine Chemical Corp. (Mitsubishi, Asahi Denka)	Jay Kolaya Website MSDS	RUP – 110GP	Magnesium-zinc: magnesium compounds trade secret (<80%) Zinc stearate (< 20%) Inorganic compounds trade secret (< 10%) Organic compounds trade secret (<10%)	For automobile PVC wire harness.
Amfine Chemical Corp. (Mitsubishi, Asahi Denka)	Jay Kolaya Datasheet MSDS	RUP – 144 RT	Magnesium-zinc: Inorganic compounds trade secret (< 75%) Zinc stearate (< 25%) Organic compounds trade secret (< 20%)	For automotive PVC wire harnesses and UL building wires (such as THW-2 and THWN-2) requiring long term wet properties.
Arkema (previously Atofina)	Peg Duffy Additives Customer Service	Stavinor	Calcium-zinc	Product no longer manufactured in the U.S., and is only available for purchase in Europe.
Associated Additives	Ingrid Lane Datasheet MSDS	Almstab PCZ4	Zinc stearate and calcium stearate	Can replace liquid cadmium-barium-zinc systems. Typical loading levels are 4 t0 6 phr. Would need to be modified for use with wire and cable applications.
Baerlocher		Baeropan, Baerostab		
Blachford	Howard Gunn	Chemstab	Barium-zinc	Products no longer manufactured.
Chemson	Sent email	Naftomix, Naftosafe	Calcium-zinc, magnesium-aluminum-zinc, organic based stabilizers?	

Table 3.4.4 R: List of Mixed Metal Heat Stabilizers:

Manufacturer	Data Source	Model	Chemical (s)	Performance
Chemtura (GL and Crompton)	Marge Biercevicz MSDS Website	Mark EZ 760	Magnesium/aluminum/zinc: Isopropylidenediphenol (< 20%) zinc stearate (< 15%) magnesium aluminum hydroxide carbonate CAS 11097-59-9 (? %)	Mark EZ 760 is a low zinc containing solid stabilizer specifically developed to meet the general requirements of PVC cable insulation compounds, e.g. heat stability and volume resistance, as well as excellent low water absorption properties. This product is also suitable for flame retarded and transparent formulation.
Chemtura (GL and Crompton)	Marge Biercevicz MSDS Website	Mark 6731	Barium/zinc: Barium stearate (< 50%) Metal oxide trade secret (< 25%) Metal oxide trade secret (< 20%) Zinc stearate (< 12%) Trade secret (< 5%) calcium silicate (< 5%)	When used with Drapex® 6.8, epoxidized soybean oil, Mark 6731 can be used as a replacement for lead and cadmium containing stabilizers in wire and cable jacketing and primary insulation compounds.
Chemtura (GL and Crompton)	Marge Biercevicz MSDS Website	Mark 6750	Calcium/barium/zinc: Calcium hydroxide (45 – 55%) Barium stearate (20 – 30%) Zinc stearate (10 – 20%) Titanium dioxide (5 – 10%) Trade secret (? %)	Used for flexible wire and cable jacket compounds. Mark 6750 is a highly efficient powder stabilizer intended to replace lead stabilizers in UL-62, UL-444, UL-493 and UL-719 jacket compounds. Mark 6750 imparts excellent early color hold and long term dynamic stability. Where solid Barium/Cadmium stabilizers are used, Mark 6750 can be substituted resulting in equivalent color hold and improved long term stability.

Table 3.4.4 R: List of Mixed Metal Heat Stabilizers:

Manufacturer	Data Source	Model	Chemical (s)	Performance
Chemtura (GL and Crompton)	Website	Mark 6736 ACM	Barium/zinc: Barium stearate (< 45%) Metal oxide trade secret (< 20%) Zinc stearate (< 20%) Titanium dioxide (< 15%) Hydrotalcite trade secret (< 10%) Trade secret (< 5%) Calcium silicate (< 5%) Metal oxide trade secret (< 2%) Zinc compound (< 1.5%)	Designed as a replacement for conventional lead heat stabilizers for wire and cable primary insulation compounds. Compared to leads, Mark 6736ACM will improve the early color hold of the insulation compound. In addition long-term heat stability will be better than a previously available barium/zinc stabilizer. Mark 6736ACM imparts electrical properties to insulation compounds only slightly less than that of lead stabilizers.
Chemtura (GL and Crompton)	Website	Mark 6751	Calcium/barium/zinc: Calcium hydroxide (45 – 55%) Barium stearate (20 – 30%) Zinc stearate (10 – 20%) Titanium dioxide (5 – 10%) Trade secret (?%)	Used for flexible wire and cable jacket compounds, and is intended to replace lead stabilizers in UL-62, UL-444, UL-493 and UL-719 jacket compounds. Mark 6751 imparts excellent early color hold and long term dynamic stability. Where solid Barium/Cadmium stabilizers are used, Mark 6751 can be substituted resulting in equivalent color hold and improved long term stability.

Table 3.4.4 R: List of Mixed Metal Heat Stabilizers:

Manufacturer	Data Source	Model	Chemical (s)	Performance
Chemtura (GL and Crompton)	Website	Mark 6767	Calcium/barium/ magnesium/zinc: Calcium hydroxide (<45%) Magnesium oxide (<15%) Titanium dioxide (<15%) Barium carboxylate trade secret (< 12%) Barium carboxylate trade secret (< 12%) Calcium silicate (< 8%) Antioxidant trade secret (< 8%) Trade secret (< 6%) Zinc carboxylate trade secret (< 5%) Zinc carboxylate trade secret (< 4%)	Used for flexible wire and cable PVC compounds, and is intended to replace lead stabilizers in UL-62, UL-493 and UL-719 jacket and insulation compounds. Mark 6767 is cost competitive with lead stabilizers in simple jacket compounds at lower loadings. The pound-volume cost will be virtually the same.
Chemtura (GL and Crompton)		Mark 6796	Calcium-zinc	
Chemtura (GL and Crompton)		Mark 6797	Calcium-zinc	
Chemtura (GL and Crompton)		Mark 6784 ACM	Calcium-zinc	
Durachemicals		Durastab	Calcium-zinc	
Ferro		Therm-chek RC 149, 216, 197, 215, 217	Great article	
Ferro	Datasheet	Therm-chek PD 958 P	Calcium-zinc	Developed as a replacement for lead-based heat stabilizers in wire and cable formulations. Useful in general jacketing applications, that do not require wet electrical properties

Table 3.4.4 R: List of Mixed Metal Heat Stabilizers:

Manufacturer	Data Source	Model	Chemical (s)	Performance
Ferro	SpecialChem	Therm-Chek RC 376P and RC 377P	Calcium-zinc	Designed to replace tribasic lead sulfate on a part for part basis in general purpose wire and cable jacketing applications.
Ferro		Therm-Chek SP1797	Barium/cadmium/zinc	Used for flexible PVC extrusion applications.
Ferro		Therm-Chek MX 125	Barium/cadmium/zinc	Used for flexible PVC extrusion applications.
Ferro	SpecialChem	Them-Chek RC 556P	Calcium-zinc	Replacement for lead-based heat stabilizers in general purpose jacketing and insulation applications that do not require wet electrical properties. Does not require ESO as a co-stabilizer.
Ferro	Jim Keenan Datasheet	Therm Chek 7206	Calcium-zinc	Used for a wide range of cable applications including energy and telecommunications. Used for both primary insulation and sheathing. Designed to have processing characteristics similar to those of lead. The dosage for sheathing and low temperature cables is 3 – 5 phr.
Ferro	SpecialChem	Therm-Chek 7208P	Calcium-zinc	Used for hight temperature cable and automotive wire applications. Suitable for use in 105 degree Celsius rated automotive and UL insulation products.
Ferro	Jim Keenan Datasheet	Therm Chek 7209	Calcium-zinc	Used for a wide range of cable applications including energy and telecommunications. Used for both primary insulation and sheathing. For some applications the level of lubrication may need to be adjusted. The dosage for sheathing and low temperature cables is 3 – 5 phr.
Ferro	Jim Keenan Datasheet	Therm Chek 7700	Aluminum-magnesium-zinc	Used for high temperature cable and automotive wire applications. Designed to have processing characteristics similar to those of lead. Outperforms lead in the Congo Red test. Compounds stabilized with this product exhibit lower levels of water absorption than compounds stabilized with calcium-zinc stabilizers. Recommended dosage is 7 – 12 phr.

Table 3.4.4 R: List of Mixed Metal Heat Stabilizers:				
Manufacturer	**Data Source**	**Model**	**Chemical (s)**	**Performance**
Halstab		Plastistab		
Kyowa (Kisuma)	K. Kakinuma, Robert Groenhagen Datasheet MSDS	Alcamizer P93	Magnesium zinc aluminum hydroxide carbonate hydrate, CAS 169314-88-9, (95 - 100%) MgO/Al_2O_3 Molar ratio: 3 ZnO/Al_2O_3 Molar ratio: 1	No deterioration of the insulating characteristics of PVC.
Kyowa (Kisuma)	K. Kakinuma, Robert Groenhagen Datasheet MSDS	Alcamizer 1	Magnesium aluminum hydroxide carbonate hydrate, CAS 11097-59-9, (95 – 100%) MgO/Al_2O_3 Molar ratio: 4	No deterioration of the insulating characteristics of PVC.

3.4.4.5 Assessment Summary

The following table summarizes the alternatives assessment information for lead heat stabilizers.

Table 3.4.4 S: Assessment Summary of Alternative Heat Stabilizer Constituents for PVC Wire and Cable Coatings

Assessment Criteria		Lead (Reference)	Comparison Relative to Lead				
			Zinc stearate	Barium stearate	MgAlZn	MgAl	Titanium dioxide
Environmental Criteria	Toxic to Aquatic Species	Yes	+	+	+	+	+
Human Health Criteria	Carcinogenicity	EPA B2 IARC 2B	+	+	+	+	=
	Developmental Toxicity	Yes (Prop 65)	+	+	+	+	+
	LD 50 (oral dose rats)	> 2,000 for tribasic lead sulfate	+	+	+	=	+
	Occupational Exposure: PEL/REL (8-hour TWA)	0.050 mg/m^3 (REL)	+	+	?	+	+

Comparison Key + Better = Similar - Worse ? Unknown

3.5. Summary and Conclusions

Manufacturers use lead metal, alloys and compounds for many different products. Lead possesses the general physical properties of other metals, *e.g.,* as a conductor of electricity and heat. Lead has a low melting temperature (327° C) and extreme malleability, which enables the easy casting, shaping, and joining of lead products. The high density of lead is desirable for several product categories including weighting applications, and shielding against sound, vibration, and radiation.

Lead is used in the manufacture of batteries, metal products, cables, ceramic glazes, and various other products. Exposure to lead can occur from breathing contaminated workplace air or house dust or ingesting lead-based paint chips or contaminated dirt. Lead is a very toxic element, causing a variety of effects at low dose levels. Brain damage, kidney damage, and gastrointestinal distress are seen from acute (short-term) exposure to high levels of lead in humans. Chronic (long-term) exposure to lead in humans results in effects on the blood, central nervous system (CNS), blood pressure, kidneys, and Vitamin D metabolism. Children are particularly sensitive to the chronic effects of lead, with slowed cognitive development, reduced growth and other effects reported. Reproductive effects, such as decreased sperm count and spontaneous abortions have been associated with high lead exposure. The developing fetus is at particular risk from maternal lead exposure, with low birth weight and slowed postnatal neurobehavioral development noted. Human studies are inconclusive regarding lead exposure and cancer.

Human exposure to lead occurs through a combination of inhalation and oral exposure, while dermal absorption of inorganic lead compounds is reported to be much less significant than absorption by inhalation or oral routes. Inhalation generally contributes a greater proportion of the dose for occupationally exposed groups, and the oral route generally contributes a greater proportion of the dose for the general population.

We looked at alternatives to the use of lead for ammunition, wheel weights, fishing sinkers, and heat stabilizers for wire and cable applications. These applications were chosen based on stakeholder input, importance to Massachusetts industry and consumers, and likely availability of alternatives. Ammunition used at indoor firing ranges has led to significant worker exposure, and at outdoor firing ranges is a source of lead contamination in the Commonwealth. Wheel weights and fishing sinkers were chosen to be representative of a large number of lead uses that rely on its high density. Wire and cable coating heat stabilization is the category with the largest use of lead among Massachusetts manufacturers.

There are uses of lead that are important to certain stakeholders that did not make the priority list for this assessment because of the time and resource constraints associated with this study. These important uses of lead, such as roof flashing and pigments, could be further investigated given additional time and resources.

Ammunition

Five alternatives were assessed for lead in handgun ammunition used at indoor firing ranges. In general, the alternatives are more desirable from a human health and environmental standpoint, with the exception of aquatic toxicity for copper and zinc. Alternatives are available that closely approximate the ballistic performance of lead ammunition and have the benefit of being frangible, which reduces the risk of injury from ricocheted bullets and reduces wear on targets. The current purchase price for alternatives is significantly higher than lead ammunition but operational costs of firing ranges can be reduced through the use of lead-free ammunition.

Wheel Weights

Four alternatives were assessed for lead use in wheel weights. In general, the alternatives are more desirable from a human health and environmental standpoint, with the exception of aquatic toxicity for copper and zinc. The alternatives meet the performance requirements for use in automobile applications and steel and zinc weights are currently used by auto manufacturers. Steel and zinc weights are competitive in price with the coated lead weights used by auto manufacturers.

Fishing Sinkers

Five alternatives were assessed for lead use in fishing sinkers. In general, the alternatives are more desirable from a human health and environmental standpoint, though there are some data gaps for the ceramic, bismuth, and tungsten alternatives which makes it difficult to make a full comparison. No one alternative meets the technical performance requirements for every sinker type or application but each alternative is successfully being used for one or more types of sinkers. While most alternatives are several times the price of equivalent lead sinkers, steel bullet weights and egg sinkers are competitive in price to the equivalent lead sinkers.

Heat Stabilizers for Wire and Cable

Five alternatives were assessed for lead use in heat stabilizers. In general, the alternatives are more desirable from a human health and environmental standpoint. Alternatives are available that meet the wire and cable technical specifications, and research on new alternatives is ongoing. The cost differential between lead and non-lead heat stabilizers is estimated to be between cost neutral and a 10% premium for mixed metal heat stabilizers. This cost differential is anticipated to diminish as mixed metal heat stabilizers gain further market acceptance and as new materials reach commercialization.

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Chapter 4. Formaldehyde

Five Chemicals Alternatives Assessment Study

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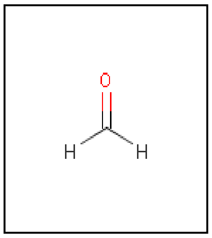
4.1 Overview



The metal catalyst oxidation process to create formaldehyde from methanol was discovered in 1868 by A. W. Hofmann. Formaldehyde's use grew rapidly throughout the 19th and 20th centuries, and formaldehyde (CH_2O, CAS#50-0-0) remains a common and important industrial chemical. Profoundly simple, inexpensive and useful, many products are made from or contain formaldehyde, including resins, permanent press fabric treatments, tissue preservatives, lawn fertilizers, cosmetics and disinfectants. Combustion of fuels and biomass is a significant source of formaldehyde in the environment. Formaldehyde is produced in animals and plants as a result of natural metabolic processes, but is rapidly metabolized through a dedicated metabolic pathway (formaldehyde dehydrogenase) (Agency for Toxic Substances and Disease Registry (ATSDR) 1999b; Liteplo et al. 2002).

Wood adhesives used to make plywood, particleboard and other manufactured wood products are the dominant end use for this chemical, accounting for 64% of the total 24 million metric tons consumed worldwide each year (Bizzari 2004). The plastics industry also uses formaldehyde-based resins extensively, especially for car parts. Because the polymerization of these resins can partially incomplete or can reverse under certain circumstances, construction materials, furniture and consumer products have been identified as sources of formaldehyde in indoor air at levels consistently higher than outdoor air, and at levels with the potential to cause health effects, such as respiratory irritation. In the early 1980's attention to high average levels in mobile homes helped bring about emission standards for formaldehyde-resin building materials that have decreased product "off-gassing." While humans have evolved to metabolize the very low levels of formaldehyde that are endogenous to human cells, at higher levels these metabolic processes are overwhelmed (Agency for Toxic Substances and Disease Registry (ATSDR) 1999b). Thus, formaldehyde can be highly toxic to humans. It has strong odor, is highly irritating, is a potent sensitizer, and has been determined by IARC, EPA, OSHA and NIOSH to be a carcinogen.

4.1.1 Characteristics of the Chemical

Formaldehyde is a gas at room temperature and is soluble in polar solvents, including water. It is easily synthesized from methanol. It has a strong irritating odor and a low odor threshold. It is colorless and flammable (Agency for Toxic Substances and Disease Registry (ATSDR) 1999a). Formaldehyde polymerizes readily with heat which makes it especially useful in resin production, and especially expensive and challenging to transport. Because of these limitations, it is usually made close to where it is used and there is very little trade in pure formaldehyde. Formaldehyde is most often produced, transported and used as a 37% solution in water known as formalin. These solutions also contain a stabilizer, typically methanol (at 12%), to prevent polymerization. In the presence of air and moisture at room temperature, formaldehyde readily polymerizes to paraformaldehyde, a solid form that is also a commercial product.

Table 4.1.1 A: Chemical/Physical Characteristics of Formaldehyde
(Agency for Toxic Substances and Disease Registry (ATSDR) 1999b; Environmental Science Center 2004; Hazardous Substances Data Bank)

Characteristic	Description
Melting/Boiling Point	-92° C /-21° C
Vapor Pressure	Gas
Octanol/Water Partition Coefficient	Log Kow = 0.350
Density	0.815 g/mL at -20° C; Gas: 1.067 (Air = 1)
Solubility	Very soluble in water and polar solvents; up to 55% (freshwater at 20 °C). Soluble in alcohol, ether, acetone, benzene
Soil Sorption Coefficient	Log Koc = 1.567; very high mobility in soil
Bioconcentration Factor	3.2 (estimated based on the chemical's octanol/water partition coefficient); formaldehyde is not expected to bioaccumulate
Henry's Law Coefficient	3.27×10^{-7} atm-m^3/mol @ 25 °C
Biodegradation	Half-Life (in sunlight) 1.6-19 hours producing H_2 and CO or H^+ and HCO^-

4.1.2 Health and Environmental Impacts

Exposure and Effects on Human Health

Because formaldehyde is highly reactive, water soluble and rapidly metabolized, people may experience its toxic, irritating and sensitizing effects at the site of contact, such as the upper respiratory tract, the eyes and the skin (Liteplo et al. 2002). Such symptoms may be experienced by those exposed at their jobs, but also have been reported among students in gross anatomy labs who are exposed to formaldehyde used to preserve human and animal specimens (Kriebel et al. 2001) and occupants of mobile homes constructed largely of particleboard. (Liu et al. 1991) Inhaled formaldehyde is readily absorbed by the upper respiratory tract and can be rapidly metabolized and detoxified into formate by almost every cell in the body (Agency for Toxic Substances and Disease Registry (ATSDR) 1999b). Skin contact results in severe irritation and burns and some formaldehyde may pass through the skin, though it is unlikely to cause systemic effects due to rapid metabolism. Repeated prolonged exposures may result in sensitization of the individual to formaldehyde. Sensitized individuals are more likely to experience contact dermatitis and asthma attacks than the non-sensitized. Formaldehyde exposure may also trigger asthma attacks in individuals with underlying asthma. Headaches, chest pains, and other symptoms may also be linked to exposure to low levels of formaldehyde in indoor air. While unlikely occurrences, ingestion of formaldehyde or very high air concentrations can quickly cause death due to burning of the lungs and subsequent edema ("flooding" of the lungs).

In 2004 IARC moved formaldehyde from the 2A – probable human carcinogen group, to Group 1: sufficient evidence that it is a human and animal carcinogen (International Agency for Research on Cancer (IARC) 2004). This determination was based on several epidemiological studies. Occupationally exposed industrial workers and those handling embalming fluids or preserved tissues were found to have elevated risks of nasopharyngeal cancer. Six of seven studies of embalmers and pathologists and two of three studies of industrial workers also found excess risk of leukemia. It has been hypothesized that because formaldehyde is a natural part of the environment and humans have evolved to cope with such low level exposures, high levels of exposure are required to induce carcinogenesis (Natz 2006). ATSDR and WHO reviewed toxicology and epidemiological studies and did not conclude that formaldehyde causes adverse reproductive and related outcomes, although some animal and human studies have found reproductive or developmental effects (Taskinen et al.

1999; Zeljenkova, Szabova 2004). Formaldehyde has been found to be toxic to cells and genes (ATSDR 1999b). Human health effects are summarized in Table 4.1.2 A

Table 4.1.2 A: Human Health Effects

Acute	• Irritation of the eyes, nose, throat, and skin. • Burns. • Narrowing of the bronchi and an accumulation of fluid in the lungs. • Risk of death from severe inhalation exposure: throat swelling, chemical burns to the lungs. • Drinking as little as 30 mL (about 2 tablespoons) of formalin can cause death.
Cancer	• Nasopharyngeal cancer. Possibly leukemia and cancer of the sinuses.
Other chronic	• Sensitization: contact dermatitis and possibly asthma (case reports only) • Central nervous system depression: headache, depression, mood changes, insomnia, irritability, attention deficit, and impairment of dexterity, memory, and equilibrium. • Genotoxic: sister chromatid exchange and chromosomal aberrations. • Cytotoxic

People – workers, children, community members, building occupants – are exposed to formaldehyde through natural sources, and those that are human-made, in many contexts. The main human-made sources of exposure are summarized in Table 4.1.2 B, along with some measured exposure levels in Table 4.1.2 C. Note that many of the values reported in this table of historical exposures come from exposure studies conducted in the 1970's and 1980's; exposure levels today are expected to be lower as a result of the reduction in free formaldehyde in building products and compliance with the 1992 OSHA formaldehyde standard, which lowered permissible exposure levels in workplaces.

Table 4.1.2 B: Sources of formaldehyde exposure

Occupational	• Industrial production (resins, molding compounds, fertilizer, paper, wood products, furniture, laminates, plastics, pesticides, chemical manufacture, rubber, leather tanning, iron foundries, photographic film, textiles, scientific supply, and cosmetics) • Agriculture (sugar production, grain and seed preservative) • Oil extraction (well-drilling fluids) • Funerary work (embalming fluid) • Hospitals, laboratories and schools (preserved tissue and specimens) • Construction (manufactured wood products) • Transportation and energy (combustion) • Beauty salons (sanitizer, cosmetics)
Environmental	• Smog in the lower atmosphere • Mobile sources (exhaust from cars, trucks) • Stationary combustion sources (power plants) • Cigarettes and other tobacco products • Gas cookers and open fireplaces • Consumer products (antiseptics, medicines, cosmetics, dish-washing liquids, fabric softeners, shoe-care agents, carpet cleaners, glues and adhesives, lacquers, paper, plastics) • Indoor air in buildings made with or containing furniture made with plywood, particleboard, medium density fiberboard, oriented strand board; insulation; carpets and other flooring; adhesives • Industrial emissions and waste • Fertilizer • Foods (cheese, fumigated grains, naturally occurs in plants and animals)

Table 4.1.2 C: Historical Exposure Levels in Air

(Hazardous Substances Data Bank ; Hiipakka et al. 2001; Hodgson et al. 2002; Kriebel et al. 2001; Olcerst 1999)

Outdoor	• Rural areas 0.2 ppb; suburban areas 2–6 ppb; heavily populated area or near some industries 10–20 ppb
Non-industrial indoor	• Averages: Mobile homes: ~37 ppb; conventional homes ~14 ppb, classrooms~18 ppb; offices ~13 ppb • Funeral Homes: averages between 0.25 ppm and 1.4 ppm; occupational exposure avg 4.8 ppm • Cosmetology classroom (paraformaldehyde sterilent): 0.08 ppm
Industrial	• Permanent-press fabric plants: 0.3 ppm to 2.7 ppm • Resin manufacturing plants: 0.08-12 ppm • Plywood mills, particle-board mills, furniture factories, other wood product and paper mills: 0.07-6 ppm • Textile mills and garment factories: 0.08 to 1.6 ppm • Foundries and other industrial facilities: 0.03 to 31 • Mortuaries, hospitals, and laboratories: 0.04 to 3.4 ppm
Laboratory	• 0.70 ppm average exposure and 11 ppm highest short-term exposure for gross anatomy laboratory students

Formaldehyde has been identified as an important indoor air contaminant (Spengler et al. 2001). As part of their efforts to reduce sources of formaldehyde in indoor air, the California Air Resources Board commissioned a study of the emission rates of products and materials that contain or generate formaldehyde. At the end of the 20-hour test period, investigators measured the emission rates of products placed in special chambers where temperatures and air flows approximated "typical" indoor air conditions. The following table shows that wood floor finish can contribute significant amounts of formaldehyde to indoor air as can many common products and building materials. Materials such as particleboard that are coated or covered with an impermeable surface emit far less formaldehyde than materials without such a barrier.

Table 4.1.2 D: Formaldehyde Emission Rates from Selected Indoor Sources

(Kelly 1997)

	Typical Conditions (µg/m²/h)
wood floor finish	11,000
fingernail hardener	300
latex paint	9
Cabinet door with acid-cured finish	460
medium-density fiberboard cabinet door	360
Particle board	240
Particle board with vinyl laminate	16
softwood plywood	4
new permanent-press shirts	110
washed permanent-press shirts	42
fiberglass insulation	32

Environmental Effects

Formaldehyde is a natural component of the environment and of the human body. The main effects of formaldehyde in the environment are discussed above as human health effects from exposures that exceed "normal" levels. In outdoor or indoor air, as a combustion product, an industrial pollutant, "off-gassed" from consumer products or building materials, or in smog, formaldehyde can cause acute and chronic health problems for exposed humans. Formaldehyde biodegrades readily in air, water and soil under both aerobic and anaerobic conditions (Hazardous Substances Data Bank). It is not commonly found in drinking water and only in limited quantities in food, such as in cheeses and grains where it occurs naturally and is added to kill pathogens. Formaldehyde in the air breaks down in sunlight during the day into carbon monoxide and formic acid, a component of acid rain. In animals, formaldehyde breaks down into formate and carbon dioxide. Formaldehyde is not bioaccumulative (does not build up in plants and animals).

Occupational and Environmental Standards and Guidelines

Formaldehyde is regulated as a human carcinogen, and classified as either a probable, potential or likely human carcinogen by IARC, OSHA, NIOSH, and EPA's NTP. OSHA's 1992 comprehensive standard requires employers to limit 8-hour exposures to less than 0.75 ppm, but they must take certain protective actions if exposures reach 0.5 ppm. Exposure monitoring, medical surveillance, and medical removal, engineering controls and respiratory protection, training and labeling are some of the extensive requirements of the standard. Formaldehyde is identified as a hazardous and toxic chemical in all media by the EPA and subject to Clean Air Act MACT standards, emissions permits and special disposal requirements.

Many manufacturers of consumer and building products have been reformulating to remove formaldehyde, or improving their products and processes to inhibit the release of formaldehyde. Urea-formaldehyde foam insulation, installed in the early 1970's across North America to conserve energy, and later found to contribute to high indoor formaldehyde levels, is restricted in many states, including Massachusetts, and manufacturers have stopped producing it. Beginning in 1985, the Federal Department of Housing and Urban Development restricted the use of wood products made with formaldehyde-based resins in mobile and prefabricated homes to those that met low emission limits as determined in standardized large chamber tests. Industry groups working with government and others have developed emission standards for particleboard and plywood and codified these in several ANSI standards. These standards are similar to HUD's. As a result of these standards and voluntary efforts by industry "manufacturers have reduced formaldehyde emissions from pressed wood products by 80-90% from the levels of the 1980's," according to the U.S. Consumer Product Safety Commission (CPSC 1997). However, over 50% of particleboard products destined for the US market (*e.g.,* furniture) are made in China; it is not known if these imported materials meet emission standards.

European and California restrictions on carcinogens in cosmetics have stimulated many makers to reformulate without formaldehyde (http://www.safecosmetics.org/newsroom/press.cfm?pressReleaseID=15). Because of concerns about formaldehyde's role in indoor air pollution and its impact on Californians' health and the economy, the California Air Resources Board is considering regulations to reduce formaldehyde emissions from consumer products and building materials. In its recent report on indoor air quality, CARB's highest priority recommendation to improve indoor air quality was to replace formaldehyde-emitting wood products with lower emitting ones (California Air Resources Board 2004).

Table 4.1.2 E: Exposure/Environmental Standards and Guidelines

(California Air Resources Board 2004)

OSHA (legal limits)	PEL: 0.75 ppm (averaged over an 8-hour workshift, 40-hour workweek) STEL: 2 ppm (15 minute) Comprehensive standard: requires workplace monitoring, labeling, and training and medical monitoring and engineering controls if employees are exposed above the action level of 0.5 ppm
NIOSH (recommended limits)	REL: 0.016 ppm (10-hr TWA) Ceiling: 0.1 ppm (15-minute) IDLH: 20 ppm Potential occupational carcinogen
ACGIH (recommended limits)	TLV®: Ceiling limit 0.3 ppm A2: Suspected human carcinogen
AIHA ERPG-2 (emergency response planning guideline)	10 ppm (1 hour)
EPA	Hazardous Air Pollutant under CAAA; hazardous waste under CERCLA, RCRA; hazardous substance under CWA; Federal drinking water guidelines: 1000 ug/l; Classification B1 probable human carcinogen
FDA	Food additive permitted in feed and drinking water of animals.
NFPA	(As 37% formalin liquid, no methanol): Health = 3; Flammability = 2; Reactivity = 0
HUD	Particleboard materials shall not emit in excess of 0.3 ppm; plywood 0.2 ppm measured in ASTM large chamber test
OEHHA* Chronic Reference Exposure Limit (based on irritant level)	27 ppb in indoor air over 8 hours
ANSI/Industry voluntary standards	Particleboard flooring: 0.2 ppm limit; other wood products 0.3 ppm

Table 4.1.2 E: Exposure/Environmental Standards and Guidelines

(California Air Resources Board 2004)

Carpet and Rug Institute (voluntary standard)	Carpets 0.04 ppm

4.1.3 Use and Functionality

Formaldehyde is a basic building block chemical and it finds its way, either directly or in derivative chemicals, into almost all sectors of the economy and thousands of products (Bizzari 2004). Over 24 million metric tons (26 million US tons) of formaldehyde were consumed in the US in 2003. Wood adhesives take the greatest share of production. Overall, US formaldehyde production has remained mostly flat as growth in formaldehyde-based products moves overseas, principally to China. Certain uses, such as in textile coatings and alkyd paints, are declining due to environmental concerns or increasing imports of pre-coated fabric. Major US uses of formaldehyde are summarized in Table 4.1.3.

Formaldehyde's readiness to polymerize makes it ideal for the production of resins that are durable, even in wet environments. The wood adhesives industry has made the greatest use of formaldehyde, accounting for 64% of formaldehyde consumed in the US. Plywood and other products that are "exterior-grade" or need to withstand wet conditions are usually made with the dark red phenol-formaldehyde resin. Hardwood plywood, particleboard and medium density fiberboard, often used for making furniture and cabinetry, are made with less expensive and higher-emitting urea-formaldehyde resins. Melamine-formaldehyde resins are also used in wood products and laminates and also molded plastic parts as are polyacetal resins. These resins are also formulated for giving specialty coatings to paper and fabrics.

Another important use for formaldehyde, (although not a large share of formaldehyde consumption), is as a sterilant and tissue preservative. Animal specimens used in high school and college biology classes traditionally have been fixed and preserved in formalin. In addition to its use in educational specimens, formaldehyde is the tissue preservative of choice for human and animal tissue preservation in medical and scientific laboratory settings. Formaldehyde is used by embalmers, and other funerary workers, who preserve human remains for burial. Formaldehyde is also used in small amounts as a pesticide in products such as latex paint and cosmetics. Its excellent disinfection properties are also made use of in paraformaldehyde salon disinfectants and in fumigants for grain and seeds.

Several commercially important chemicals are derived from formaldehyde including 1,4-butanediol (used to make polyurethane and spandex fibers), MDI, aminopolycarboxylic acids (*e.g.*, EDTA) used in cosmetics and as chelating agents, pesticides and lawn fertilizer; and "permanent-press" and flame retardant textile coatings. Interestingly, the leading substitute for formaldehyde in wood adhesives is methylene diisocyanate (MDI), which is made from formaldehyde. Additionally, 1,4-butanediol, 70% of which is made from formaldehyde, is the feedstock for the making of n-methyl pyrrolidone (nMP), a common chlorinated solvent substitute.

Many consumer products and cosmetics have added formaldehyde as resins and to kill microbes. Cosmetics that may include formaldehyde include: nail polish and hardeners (used as a film-forming resin), cuticle softener, shampoos and other hair preparations, suntan and dry skin lotions, makeup, mouthwashes, bath products, deodorants, and shaving cream. Household cleaning products that may include formaldehyde include: cleaners, dishwashing liquids, fabric softeners, shoe care agents, car shampoos and waxes, and carpet cleaning agents. Latex paint may also contain formaldehyde or formaldehyde precursors (ATSDR 1999b). Many "green" building products are made with formaldehyde resins including bamboo and cork flooring and particleboard substitutes made with agricultural waste (Greenseal).

Table 4.1.3 A: Formaldehyde Uses in the US

Major Use Category	Product Category	Uses/Applications
Resins	Urea-formaldehyde resin (23% of US consumption of 37% formaldehyde)	Wood Adhesive (particleboard, medium-density fiberboard, hardwood plywood and waferboard: Internal, non-structural applications)
		Glass fiber roofing mats
		Molding compounds: Ball milling
		Molding compounds: electrical switches, circuit breakers and other
		Cross-linking agent for surface coating including flame retardants
		Other: Low-pressure laminates, wet strength additives and coatings for paper products, textile treating, cross-linking agents for surface coating
	Phenol-Formaldehyde resin (17%)	Wood adhesives (plywood, oriented strand board (OSB), hardboard, molded wood, particleboard); Structural applications; wet strength
		Insulation (phenolic foam insulation, binders for insulation)
		Decorative and Industrial (circuit board and personal computers) laminates
		Foundry mold binders
		Molding compounds
		Other: clutch facings, disk brake pads, automatic transmission components and brake linings, protective coatings (food containers), rubber processing additives, and abrasives for metal finishings
	Polyacetal resin (13%)	High performance plastic parts for automobiles, industrial machinery, plumbing, appliances, tools, and consumer goods such as ski bindings, knife handles
	Melamine-formaldehyde resin (3%)	Adhesive in decorative laminates, OSB, plywood, mdf, particleboard
		Thermoset surface coatings
		Molding compounds such as dinnerware (medical products, household fixtures), tire cord and ceiling tiles
		Paper and textile treating (wallpaper, wrinkle resistant clothing)
		Used as cross-linking agent for flame retardant
	Coating resins (7%)	Pentaerythritol (5%) is used to make alkyd resins in solvent-based paints and finishes; Trimethylolpropane and trimethylolethane impart UV and chemical resistance to coating resins; Polyhydric Alcohols (Polyols) are alkyd resins for use in automobile paint, house paints, artists' oil paints and synthetic lubricant markets
Disinfectant/ Sterilant/ Preservative	Paraformaldehyde	EPA registered disinfectant, "Steri-dri"sanitizer and fungicide for barber and beauty and for households, ships, bedding, clothing, nonfood/non/feed transporting trucks

Table 4.1.3 A: Formaldehyde Uses in the US

Major Use Category	Product Category	Uses/Applications
	Formalin	Microbiologically active against bacteria, fungi, bacterial spores, many viruses: 8% solution with isopropanol: bacteriacidal, tuberculocidal and sporicidal 6-8% solution: sterilant 1-8%: low to high level disinfectant
		Embalming fluid
		Tissue fixation/Pathology
		Antimicrobial used in cosmetics, metal working fluids, latex paint and low VOC paint; secondary oil recovery
Derivative Chemicals	1,4-Butanediol (10%)	Used to make tetrahydrofuran (THF); urethane elastomers (spandex); gamma-butyrolactone which is used to make n-methyl pyrrolidone
	Methylene diisocyanate (MDI) (9%)	Rigid and flexible urethane foams (foam boards, furniture and bedding foam);
		Wood adhesive/binders in OSB and as a formaldehyde substitute in particleboard
		Eastomers (automotive bumbers, door panels; flexible tubing and cable jacketing; gaskets)
	Hexmethylenetetramine (3%)	Thermosetting catalyst for Novolac/phenolic resins (principal use) Manufacture of RDX explosive (cylonite) Rubber vulcanization accelerators Unisolated intermediate in the manufacture of nitrilotriacetic acid
	Aminopolycarboxylic acids (EDTA and NTA), salts (3%)	Chelating agents in industrial and household cleaners and wastewater treatment
		EDTA is also a penetration enhancer in many cosmetic products
	Fertilizers	Controlled-release urea-formaldehyde concentrates for lawn chemicals
	Herbicides (2%)	Paraquat is made from pyridine chemicals
	Textile chemicals	Wrinkle resistance (UF, MF, gyloxal-UF resins); fire retardants

4.2 Formaldehyde Use Prioritization

Chemical Use in Massachusetts

Formaldehyde is not intentionally manufactured in Massachusetts, but formaldehyde and its derivatives are used here in manufacturing other materials and products. Of the 4.8 million pounds of formaldehyde reported under TURA in 2003 (uses of less than 10,000 lbs are not reported), resins manufacture accounted for 60%, chemical manufacture 39% and energy production by-product 1%. One facility in western Massachusetts, used 2.7 million pounds in urea and melamine resins used to make molding compounds (ball milling), which, in turn, are made into plastic dinnerware and other consumer products. Massachusetts companies, institutions and consumers are significant users of formaldehyde-based products made elsewhere.

Table 4.2 A: Massachusetts Companies Reporting Formaldehyde Use in 2003 (source: MA TURA Data, 2003)				
Use	**Total Used (lb)**	**Generated Byproduct (lb)**	**Shipped in OR as Product (lb)**	**Total Emissions (lb)**
TOTAL	**4,758,984**	**162,096**	**4,572,626**	**65,053**
Chemical intermediate (dispersant)	505,794	828	504,966	614
Combustion by-product	26,872	26,872	0	26,871
Organic chemical manufacturing	14,100	6	14,094	123
Embalming chemicals	768,054	7,443	767,431	510
Paper resin	17,000	8,400	8,400	6,300
Byproduct of LNG liquification/vaporization	16,540	16,540	0	16,540
Resin and resin-coated fabric manufacture	41,366	21,694	19,671	599
Molding compounds (resins)	2,732,087	2,023	2,730,064	2,023
Electroless copper solution manufacturing	530,000	9,900	528,000	10
Electroless copper for printed wiring boards	40,727	1,179	0	728
Resins, coatings, laminates*	Trade secret	770	Trade secret	770

(*TURA quantities not available due to trade secret claim)

Table 4.2 B: Massachusetts Companies' Use of Formaldehyde in 2003
(source: MA TURA Data, 2003)

Use	% of Total
Chemical intermediate (dispersant)	16.4%
Combustion by-product	0.6%
Organic chemical manufacturing	10.8%
Embalming chemicals	0.3%
Paper resin	0.4%
Byproduct of LNG liquification/vaporization	0.4%
Resin and resin-coated fabric manufacture	0.9%
Molding compounds (resins)	58.2%
Manufacture of electroless copper solutions for printed wiring board industry	11.3%
Electroless copper for printed wiring boards	0.9%
Resins, coatings, laminates	(Claim Trade Secret)

Summary of Stakeholder Input

Stakeholders were particularly concerned with "emissive" uses of formaldehyde: manufacture and use of products with potential exposures to workers, consumers and children. The stakeholders reviewed the major use categories and types of uses including industrial, commercial, consumer and school settings. Due to concern about health effects related to indoor air exposures, stakeholders were interested to learn about alternatives to formaldehyde in building products. Formaldehyde in school settings and small businesses was also highlighted as a high priority. These settings took precedence over other larger volume uses. Wood floor finishes have been reported to emit significant amounts of formaldehyde, but manufacturers stated that no formaldehyde is added to the finishes and stakeholders prioritized uses where formaldehyde was an ingredient.

Priority Uses

Using the previously described stakeholder priorities, and the criteria listed in Section 2.3.3, uses that were representative of the major formaldehyde use categories in Table 4.1.3 were evaluated for further study. From the resin and building materials category, particleboard/wood building panels are a large use of formaldehyde in Massachusetts, with significant exposure potential for construction workers and building occupants. In addition, these panels were identified as a very high priority for stakeholders. Urea-formaldehyde resins used in fiberglass insulation, were designated as a secondary choice. In the disinfectant and consumer category, stakeholders placed a high priority on the use of paraformaldehyde sterilants, currently required by the Massachusetts Board of Cosmetology. Salon patrons, workers and students in cosmetology classes are exposed to this formaldehyde source. Stakeholders indicated that exposures experienced by children were a very high priority, leading to the selection of formaldehyde use in preserved educational specimens. Textile finishing chemicals (formaldehyde derivatives) were designated as a secondary choice, if resources became available.

The resulting high priority uses for formaldehyde were:

- Sanitary Storage in Barbering and Cosmetology
- Preserved Educational Specimens for Dissection
- Building panels

Secondary priorities, if resources had become available, were textile permanent press finishes and fiberglass insulation binders.

4.3 Formaldehyde Alternatives Prioritization

Given the limited time span and scope of this project the Institute searched for alternatives to formaldehyde for the high priority uses that seemed most feasible. Potential alternatives would be more likely to be feasible if they contributed positive values to the criteria listed in Section 2.4.3.: performance, availability, manufactured in Massachusetts, cost, environmental health and safety, and global market effect.

4.3.1 Alternatives Associated with Sanitary Storage in Barbering and Cosmetology

The Massachusetts Board of Cosmetology establishes requirements for sanitation in beauty salons. Their regulations include three references to formaldehyde. In section 3.03 of the regulations (Equipment and Hygiene Procedures), item (17) says: “One of the following methods must be used to sanitize instruments and equipment after use on any patron or model:

(a) Physical Agents.

1. Boiling water at 212°F for 20 minutes.
2. Steaming dry heat.
3. 70% grain or denatured alcohol for at least ten minutes.
4. Ultraviolet (UV) rays in an electrical sanitizer.

5. Immersion in 10% formalin for at least ten minutes.

(b) Chemical Agents.

1. Antiseptics and disinfectants (hospital grade required).
2. Vapors, formalin and steri-dry."

A bleach solution is also offered as an alternative. Item (18) says: "(a) In cosmetology salons, there must be at least two covered waste receptacles and at least one air-tight container for storing sanitized instruments. Dry sanitizer must be used in drawers." Dry sanitizer is para-formaldehyde dry sterilant, known by the trade name, "Steri-Dry." The perforated plastic containers containing the solid form of formaldehyde "leak" formaldehyde as it de-polymerizes naturally into formaldehyde gas, filling the tool boxes, cabinets and drawers where hair brushes are kept, and entering the salon and classroom air as drawers are opened.

Alternatives to use of formalin for disinfection in salons and schools were not evaluated. Alternatives are generally used, including the popular blue Barbicide disinfectant solution. Evaluation of overall proper procedures for disinfection, and testing of disinfectants' relative effectiveness was beyond the scope of this report.

Available Alternatives

While salons generally select non-formalin chemistries for the disinfection of instruments, the Board's requirement to use dry sanitizer in drawers and student tool boxes has meant that formaldehyde is present in salons and cosmetology training schools, including vocational high schools. The alternative to this use is either the use of another dry sterilant or alternative procedures that do not require use of a sterilant in storage cabinets. No alternative chemical dry sterilants were identified for use in storage drawers to "maintain" disinfection. An additional alternative is for brushes and combs and other beauty implements to be stored in an ultra-violet light cabinet where the UV light source would kill pathogens on exposed surfaces. In summary, the following available alternatives were identified:

- Process change to eliminate the need for dry drawer sterilants
- UV light cabinets for storage

Alternatives Screened Out

No alternatives were screened out because they were carcinogens, PBTs or TURA SAB more hazardous chemicals.

Priority Alternatives for Salon Disinfection and Storage

The priority alternatives for use of para-formaldehyde dry sterilants in sanitary storage are

- Process Change: Storage of implements in a disinfected, dry, covered container and isolated from contaminants
- UV light cabinets for sanitary storage

4.3.2 Alternatives Associated with Preserved Educational Specimens for Dissection

High school and college students in anatomy classes dissect preserved specimens, including fetal pigs, frogs, cats, sharks and other species, to learn from their direct experience of the animal's anatomy. Traditionally, educational specimens have been preserved with a formalin solution to prevent the natural decay of the tissues. Formaldehyde both kills the bacteria that would decay the tissue and it polymerizes the tissue to maintain, to some degree, its texture, structure and color. Formaldehyde off-gasses during the period of time of the storage, use and disposal of the specimen. Students, lab instructors and technicians are exposed to formaldehyde through their repeated contact with these specimens. Smaller animals are usually dissected within a couple of weeks, but larger animals, such as cats, might be used by students over two semesters.

Specimens are ordered by schools from scientific supply companies that specialize in providing preserved specimens for educational and scientific uses. Specimens are first "fixed" with a fixative (traditionally, formalin) and then may be sold with a holding solution that may be formaldehyde, or some other preservative such as propylene glycol. Specimens fixed with formaldehyde may be repeatedly washed by the vendors to remove as much formaldehyde as possible prior to shipment. They may then be placed in a "humectant" such as propylene glycol, to keep them from drying out. In addition to specimen sales, scientific supply companies also sell fixative and holding solutions to be used by researchers and advanced students who preserve their own specimens or who maintain specimens long term in jars. In response to consumer demand, scientific supply companies have developed their own formaldehyde-free fixatives, specimens and holding solutions. Formaldehyde-free alternative specimens are evaluated here, as well as the technological alternative of video and virtual dissection.

Available Alternatives

The Institute evaluated specimens fixed and preserved in alternative solutions available for purchase by educators, rather than the solutions themselves. Specimens did not appear to be available in the following alternative preservatives: Carnoy's Solution made of ethyl alcohol, chloroform and acetic acid; "Prefer" made of ethyl alcohol and glyoxal; Ultrum II Tissue Fixative made of water, sodium acetate, zinc chloride and glutaraldehyde; as well as Caro-Safe Preservative, NOTOXhisto, Nebanol Concentrate and phenoxyethanol solutions. Thus, these alternative preservatives were not evaluated. A complete list of available alternatives and their ingredients is included in Appendix C.

The following alternatives were identified:

- specimens preserved in Formalternate by Flinn Scientific
- specimens preserved in Wardsafe by Ward Scientific
- specimens preserved in S.T.F. (Streck Tissue Fixative) Preservative by Nebraska Scientific
- specimens preserved in Carolina Biological Supply's Carolina's Perfect Solution®
- unpreserved specimens
- video/virtual dissection

Alternatives Screened Out

Specimens fixed with formalin (typically 37% formaldehyde, a carcinogen, and 12% methanol), were excluded even if they were sold or maintained in holding or preserving solutions that were formaldehyde-free. Maryland State Anatomical Solution and Bouin's Fixative Solution contained formaldehyde and were screened out.

Priority Alternatives for Educational Specimens

Because Carolina Biological Supply did not provide a description of the proprietary ingredients, the Institute did not evaluate specimens in Carolina's Perfect Solution® (technical review is available in Dr. Foxall's report to the Institute). The alternative of dissecting live or recently deceased, unpreserved specimens was also excluded for legal, ethical and practical reasons.

Three specimen alternatives and video/virtual dissection were selected as high priority alternatives for assessment. Due to limited time, only one specie was evaluated for each. Other species may be preserved in different chemical mixtures of the same fixative. For example, Ward's fetal pigs are preserved in "WardSafe" (glutaraldehyde, propylene glycol, ethylene glycol phenyl ether, diethylene glycol phenol ether) but the product contains different ingredients to the frog's "WardSafe" (gluteraldehyde). The three alternative-preserved specimens were grass frogs preserved in

- Formalternate by Flinn Scientific,
- Wardsafe by Ward Scientific, and
- S.T.F. (Streck Tissue Fixative) Preservative by Nebraska Scientific.
- Virtual/video dissection

Formalternate is a combination of propylene glycol, ethylene glycol phenyl ether and phenol. Wardsafe is primarily glutaraldehyde. S.T.F. is diazolidinyl urea, 2-Bromo-2-nitropropane-1, 3-diol (Bronopol), zinc sulfate, and sodium citrate.

4.3.3 Alternatives Associated with Building Panels

Adhesives used to make plywood, particleboard and other manufactured wood products account for 64% of the total 24 million metric tons of formaldehyde consumed worldwide each year (Bizzari 2004). Building panel boards designed to withstand loads even when wet are designated as "structural use panels" and include exterior- and interior-grade softwood and hardwood plywood and oriented-strand board. Structural use panels' uses include exterior sheathing, roof decking, and floor decking. Particleboard, medium density fiberboard, and hardwood plywood are primarily used for furniture, shelving, built-in furniture and cabinetry, and interior decorative paneling and flooring. Softwood plywood or oriented strand board (OSB) may be used for carpet and tile underlayment and some built-in furniture and cabinetry that requires less visual appeal and durability. (The red-black color of phenol-formaldehyde resin prevents it from being used in high-end decorative applications.)

While certain types of panels are primarily used for certain uses, they may substitute for each other at times, and softwood plywood, in particular, is quite versatile. As for substitutes that may replace wood panels made with formaldehyde-based resins, the potential substitutions are limited at this time, but, as is described below, that may change in the near future. Many factors influence the choice of materials for building including design and aesthetic considerations, technical specifications, environmental and health considerations, availability and price. Substitutes may match the expectations laid down by traditional products, or they may create new market niches, providing new qualities and stimulating new designs, specifications, and acceptable prices. Growing demand for "green" building products may also influence where and how these panels will be used. Additionally, use of alternative binders, such as the relatively benign polyvinyl acetate (PVA) glue, which is currently used on a special order basis because of its expense, may expand. Finally, "greener" resin technologies that are in the research and development stage may be commercialized in the next few years.

Available Alternatives

The following types of alternatives to formaldehyde-resin based wood panels were identified:

- "low emitting" phenol formaldehyde resin panels
- MDI (methylenediphenyl diisocyanate) based resin panels
- panels made with cement, sand and wood fibers
- Columbia Forest Products soy-based resin hardwood veneer core plywood panels
- Homasote's recycled paper panel boards
- Viroc's wood fiber-Portland Cement panels
- JER EnviroTech's plastic-wood fiber panel

Late in our review the Institute learned that PVA glue is used on a special order basis by many hardwood plywood manufacturers, especially for architects building interiors to the U.S. Green Building Council's Leadership in Energy and Environmental Design (LEED) specifications. Points under the LEED system are awarded for composite wood products that do not use urea-formaldehyde resins. PVA glue is a water-based synthetic latex glue that is used extensively in furniture and laminate manufacture. It is known as white or yellow glue (*i.e.*, Elmer's or carpenters' glue). It can be used with the equipment and processes that currently are used to make panels with urea-formaldehyde resins and has excellent performance characteristics for interior and possibly some exterior applications. It is relatively non-toxic with the exception of a very small amount of un-reacted vinyl acetate monomer (0.4%). Vinyl acetate is an animal and possible human carcinogen, an irritant and a cause of heart problems and other systemic effects in humans (Hazardous Substances Data Bank). Some PVA glues are enhanced with an isocyanate catalyst (isocyanates are sensitizers and can cause asthma and dermatitis). PVA-based panels do not appear to be advertised or readily commercially available. PVA is more expensive than urea-formaldehyde resins.

Alternatives Screened Out

Two categories of alternatives were screened out: "lower-emitters" of formaldehyde and products made with other hazardous chemicals. The "low-emitters," principally products made with phenol-formaldehyde that meet ANSI emissions standards, were excluded because they are made with formaldehyde and still emit low amounts during use. Therefore, they did not pass the carcinogenicity screen. Wood products may also generate formaldehyde as a natural process; products made with no "added" formaldehyde are evaluated here.

Some companies are producing boards made with polyurethane adhesives based on methylenediphenyl diisocyanate (MDI) in place of formaldehyde-based resins. MDI did not pass our initial health and safety screen because it is on the TURA SAB "more hazardous chemical list" due to its acute toxicity and sensitizing properties (Toxics Use Reduction Institute (TURI)). Additionally, while lifecycle issues are not a major focus of this study, MDI is made from formaldehyde. A popular product made with a combination of Portland cement, silica sand and wood fibers was also screened out because of the significant amount of crystalline silica, an IARC Group 1 carcinogen, in the product. These products represent no known environmental threat or risk to building occupants, but significant silica dust is generated during construction activities. Forest Stewardship Council certified-sustainable wood or "agrifiber" composite panels are "green" products that were not included because they use either phenol-formaldehyde resins, MDI or similar resins (see for example http://www.agriboard.com/index.htm).

Priority Alternatives for Alternative Panels

The four remaining alternatives were identified as high priority for assessment as alternatives for formaldehyde resin-based building panels. The first of these is a hardwood veneer core plywood panel that could directly substitute for the equivalent traditional product used to make cabinets, built-in furniture, paneling, shelving, doors and other uses requiring a high end wood product. This alternative is Columbia Forest Product's PureBond panel made with a soy-based resin. This was the only alternative that used an alternative resin. (The other three products are formed by different processes.)

Two other products that were evaluated may substitute for plywood or OSB in building sheathing, roof decking or floor decking. They are Homasote's recycled paper panel boards and Viroc's wood fiber-Portland Cement panels. The fourth product, JER EnviroTech's plastic-wood fiber panel, is an "emerging technology" and may substitute for particleboard and possibly for structural uses as well. Four specific manufacturers' products were evaluated although similar products may be made by other companies. For example, another recycled paper board is ThermoPly by Covalence Coated Products (see http://www.covalencecoatedproducts.com/pages/thermoply.html). The selection of particular representative products does not constitute an endorsement by the Institute, or imply that other similar products are not worthy of further assessment.

Columbia Forest Product's PureBond veneer core plywood was a high priority for assessment because it was the only traditional type of product that used an alternative resin and that passed the screen.

In addition, there was a great deal of stakeholder interest in this product. PureBond is made with soy flour and a resin manufactured by Hercules Chemical called Kymene® 624 Wet Strength Resin. The resin is a cationic amine polymer-epichlorohydrin amine called polyamide-epichlorohydrin (PAE) and it is widely used in as a wet-strength resin in paper and textile manufacturing. Epichlorohydrin has been determined to be an animal and a probably human carcinogen by IARC and EPA's NTP Program and has several other serious potential health and environmental hazards. Epichlorohydrin is not listed on the Hercules' MSDS for Kymene® 624 nor is it listed on the PureBond MSDS. According to the manufacturer and the EPA, epichlorohydrin is completely consumed in the batch manufacturing process used to make the resin. There are no emissions from this process and no residual or "free" epichlorohydrin in PAE where it is irreversibly transformed in the polymer matrix (Steib 2006; USEPA 1984). Despite the lack of potential for worker, consumer or environmental exposure to epichlorohydrin during PureBond building panel manufacture, use or disposal, the health and safety and environmental assessment of this alternative will include a review of epichlorohydrin's potential hazards.

The final list of high priority alternatives to be assessed for wood panels is as follows:

- Columbia Forest Products hardwood plywood panels made with PureBond core and laminated veneers
- Homasote's recycled paper panel boards
- Viroc's wood fiber-Portland Cement panels
- JER EnviroTech's plastic-wood fiber panel

4.4 Formaldehyde Alternatives Assessment

4.4.1 Alternatives Assessment for Sanitary Storage in Barbering and Cosmetology

Two potentially feasible alternatives to the use of paraformaldehyde were found: elimination of the process step and UV storage cabinets. The technical, environmental and health and safety and financial evaluation of these alternatives follows.

Technical Assessment

Helen Peveri, the Executive Director of the Massachusetts Board of Cosmetology was interviewed about the Board's perspective on the use and alternatives for the use of paraformaldehyde dry sterilant. Ms. Peveri noted that, until recently, the Board had not been aware that paraformaldehyde was a potential hazard in salons and that they were interested in alternatives. She said that the Board required paraformaldehyde because they were concerned that hairdressers might not do a good job of cleaning and disinfecting brushes and the Board wanted to have some extra measure of security that the brushes were "clean." Ms. Peveri felt that the opening and closing of the drawer and putting used brushes back in would contaminate the brushes.

Denise Graham, Senior Director of Public Policy for the Association for Professionals in Infection Control and Epidemiology was consulted for the infection control perspective. Ms. Graham stated that she was unaware of guidance or requirements specific to beauty salons. Two industry groups were consulted. Both the Professional Salon Association and the National Accrediting Commission of Cosmetology Arts and Sciences said that they had no guidance, special concerns or other comments on the issue.

To represent the perspective of salon regulators and to determine best practices in infection control in salons, the Institute consulted Sue Sansom, of the Arizona Board of Cosmetology and Chair of the Health and Safety Committee of the National-Interstate Council of State Boards of Cosmetology. The National-Interstate Council's (NIC) mission is to establish best practices, standards and uniform requirements for Boards of Cosmetology and cosmetology exams in the United States is composed of members of licensing boards of cosmetology from each of the fifty states and the U.S. territories. Ms. Sansom stated that she was unaware of any state requiring use of paraformaldehyde. According to the NIC, formaldehyde-based dry sterilants are not recommended due to their carcinogenic potential. In place of dry sterilants, the NIC recommends an alternative procedure of proper cleaning, wet disinfection, drying and storage. NIC's Infection Control standard for dry storage is "Disinfected implements must be stored in a disinfected, dry, covered container and be isolated from contaminants" (National-Interstate Council of State Boards of Cosmetology).

Ms. Sansom was also consulted on the use of UV sanitizers. Ultraviolet sanitizers can be used as dry sanitary storage, but she felt that they were an unnecessary expense and "sent the wrong message" about their role in infection control. She felt that use of UV cabinets can confuse the public and the licensee by suggesting that proper disinfection is occurring when it is not.

The disinfection and storage practices recommended by the NIC are reiterated in the rules of many other Boards of Cosmetology and in the instruction offered in Milady's Standard Cosmetology – the field's primary textbook and practice guidance. This text recommends the same process iterated by the NIC: proper cleaning followed by use of U.S. Environmental Protection Agency-registered disinfectants and storage in clean, sanitized storage (Alpert 2004). Milady's Standard Cosmetology does not discuss use of dry sterilants.

The primary performance criterion by which to evaluate alternatives in comparison to formaldehyde is the ability to control harmful pathogens and to maintain sanitary storage. No studies were found that evaluate the extent of pathogen contamination, transmission and control in the salon environment. Thus, paraformaldehyde sterilant's efficacy is unknown, as is the extent of the problem of growth and transmission of harmful bacteria, etc. in salon storage and instruments.

Because instruments are required to be cleaned and disinfected and storage cabinets are also required to be cleaned and disinfected, and instruments are not to be used and then replaced in the drawers, there is minimal likelihood for potential serious contamination if these procedures are followed. For this evaluation, it is assumed that Board of Cosmetology requirements for cleaning, disinfection and hygienic storage would be followed and therefore the pathogen load in drawers would not be significant.

Given this assumption, and the input of technical experts, it was determined that the alternative of eliminating paraformaldehyde and replacing it with a process of cleaning and disinfecting of a storage container that may be placed in a drawer, or the drawer itself is technically feasible. Following cleaning (dirty surfaces cannot be disinfected), disinfection of the container may be performed with a hospital-grade EPA-registered disinfectant (as already allowed by the Board's rules). From a technical perspective, all references to formaldehyde, formalin or dry sanitizer may be eliminated from the Board's rules without any compromise of infection control as long as the correct and recommended process of cleaning, disinfecting, drying and storing is required and followed. Cosmetology inspectors may inspect such containers to insure that nothing else is stored in them and that they are clean and dry. This process also meets best practice criteria as described in the previous section. The NIC's Infection Control standard for dry storage is "Disinfected implements must be stored in a disinfected, dry, covered container and be isolated from contaminants" (California's Board of Cosmetology rules follow this process).

Ultraviolet light sanitizing cabinets are available from many sources including from the PIBBS beauty supply company (www.pibbs.com). Milady's Standard Cosmetology says that these cabinets are "useful storage containers" but will not disinfect salon implements. UV germicidal light is effective at killing pathogens, but it must strike all surfaces and this is difficult to achieve on a brush. Additionally, the cabinets may become reservoirs of pathogens if they are not regularly cleaned and disinfected, which is difficult to do given the design of the cabinets. Texas has recently revised their regulations to permit the use of UV cabinets as storage containers (83.102. Health and Safety Standards--General Requirements http://www.license.state.tx.us/cosmet/cosmetrules.htm#83106) A further performance concern is the space required for these cabinets at each station.

Financial Assessment

The elimination of paraformaldehyde will result in a modest cost savings for schools and salons (approximately $3.00 for a two ounce container that lasts six months). UV storage cabinets cost approximately $160 each. Germicidal bulbs may cost as much as $30 to replace, and there is an operating cost for energy. It is difficult to gauge the financial comparison to use of Steri-Dry, but it is estimated that the initial equipment cost and replacement bulb "operating costs" of the sanitizing cabinet would generally exceed that of using Steri-Dry.

Human Health and Safety and Environmental Assessment

Elimination of paraformaldehyde is not expected to introduce any new environmental or health and safety concerns. If the cleaning and disinfecting processes are not followed, there is a risk that elimination of use of formaldehyde in storage containers could result in contaminated brushes. However, according to experts, no other state requires use of formaldehyde in salons. The public health risk of its elimination is, therefore, likely to be very low. Massachusetts Board of Cosmetology regulations currently require the cleaning and disinfection of dry storage containers and cabinets. It should be noted that EPA-registered disinfectants may contain gluteraldehyde or quaternary ammonium compounds, both of which are sensitizers. Evaluation of safer cleaning and disinfection strategies is beyond the scope of this project but is an important related concern.

As mentioned above, UV storage cabinets may become reservoirs of pathogens if salon workers encounter difficulty in disinfecting all surfaces inside them. Exposure to UV light can cause skin cancer or eye irritation, although exposure is unlikely if the cabinet is turned off when instruments are loaded or unloaded.

Summary

From a technical, health and safety, environmental and financial standpoint, it appears feasible for paraformaldehyde to be eliminated from barbering and cosmetology drawers and cabinets.

Table 4.4.1 A: Assessment Summary for Sanitary Storage in Barbering and Cosmetology

Assessment Criteria		Steri-Dry (Reference)	Comparison Relative to Formaldehyde	
			Elimination	UV Storage
Technical/ Performance Criteria	Protects Public from Pathogens	?	=/+	-
	Meets Best Practice Guideline	**No**	+	+
Financial Criteria	Cost/yr/drawer	**$6.00**	+	-
Environmental Criteria	Hazardous Air Pollutant	**Yes**	+	+
	Drinking Water Contaminant	**No**	=	=
	Persistent/ Bioaccumulative	**No**	=	=
Human Health Criteria	Carcinogen	**Yes**	+	+
	Irritation	**Yes** (Dermal, Ocular, Respiratory)	+	+
	LD50, oral, mg/kg	rat 100 mouse 385	+	n/a
	Fire Hazard	**Yes** (NFPA 4)	+	+
	Exposure Potential	Low levels, high probability of exposure	+	+

Comparison Key + Better = Similar - Worse ? Unknown

4.4.2 Alternatives Assessment for Preserved Educational Specimens for Dissection

Because there are no published studies comparing the performance characteristics of preserved biological specimens for dissection, the Institute relied on an evaluation by an outside technical expert. Professor Thomas Foxall, Chair of the Department of Animal and Nutritional Sciences at the University of New Hampshire evaluated the alternatives with regard to their technical issues and performance. He developed criteria and used these to compare the alternatives to a formalin-preserved specimen. He used his own extensive experience in teaching gross anatomy, consultation with other anatomy teachers, his direct examination of the alternatives specimens and consultation with pathologists at the New Hampshire Veterinary Diagnostic Laboratory at the University of New Hampshire. He also evaluated a number of virtual and video dissection materials and collected cost information for all alternatives. The health, safety and environment evaluation was conducted by the Institute staff.

The following alternatives for preserved grass frogs were assessed:

- Formalternate by Flinn Scientific,
- Wardsafe by Ward Scientific, and
- S.T.F. (Streck Tissue Fixative) Preservative by Nebraska Scientific.
- Virtual/Video dissection

Technical Assessment

The main technical criteria are those that impact the educational potential of the dissection experience. Those criteria are the color, texture, and stiffness of the specimen tissue. The texture and the stiffness of the tissue directly relate to the ease of "blunt dissection," i.e., separation of the tissues without using a knife. While no preserved specimen's qualities will be true to the living animals, the preserved specimen should approximate them. Other important qualities are the odor of the specimen and whether the specimen lasts long enough for students to complete the dissection. Special handling, training and equipment requirements due to the potential hazard of the specimen are both health, safety and environment concerns and a technical concern as they impact the laboratory experience and duties of the laboratory personnel. The availability of alternatives and if they are available from reputable companies are also important considerations. Finally, a "composite" criterion representing the potential for desirable educational experience for the student was also utilized to compare the specimens. The first three criteria do not apply to video/virtual dissection.

In general, results of the expert's study showed that all of the frog specimens would be acceptable as alternatives to formaldehyde fixed animals, preserving reasonably good color, shape, size and orientation of organs so as to teach basic vertebrate anatomy. Other anatomy professors who had used alternatives were consulted and reported good experiences with them. The criteria are discussed in turn, followed by a discussion of video/virtual dissection:

Color

The color of the alternative specimens was as good as or better than the formalin-preserved specimen. S.T.F. specimen was very good; the Formalternate and Wardsafe frogs had better (more life-like) color than the formalin frog in the skin, skeletal muscle and organs.

Texture

The tissues of the frog preserved in Formalternate were the softest (softer than the formalin frog). It was pliable and easy to move organs and blunt dissect skeletal muscle. The S.T.F. frog's tissues were very soft and it was easy to move organs and blunt dissect. The Ward's frog's tissues were more hardened and less easy to blunt dissect.

Stiffness

The S.T.F. frog was the least stiff and much less stiff than the formalin frog; the Formalternate frog was also less stiff than the formalin frog. The Ward frog was rigid and more like the formalin frog.

Odor

Formalternate had no offensive or intense irritating odor; S.T.F.'s frog had a very slight "chemical" odor; and the Ward frog had an "aldehyde" odor similar to formalin.

Longevity

Longevity could not be evaluated in the timeframe of this study, however formalin will preserve specimens indefinitely. Nebraska Scientific guarantees their S.T.F. specimens for 90 days. This is within the typical timeframe of an anatomy course, but would require that specimens be ordered close to the time of the beginning of the course or dissection. The anatomy professors who had used these alternatives had not experienced problems with the longevity of the specimens as long as they were stored according to instructions (generally sealed in plastic bags).

Special Handling and Training

The alternative specimens do not require any special handling or training other than good laboratory practices. Formalin-fixed specimens may need to be disposed of as hazardous waste. These procedures may be mostly avoided with alternative specimens. With either formaldehyde or the alternatives, students must be made aware of the potential for skin reactions to chemicals and safe procedures such as washing thoroughly after dissection, not ingesting any of the specimen, and following proper storage procedures. Instructors and students should be aware that specimens in S.T.F. may release formaldehyde due to the presence of diazolidinyl urea, a formaldehyde-releasing chemical.

Availability

The alternative products are readily available from well-established companies.

Educational Value

The educational value of these alternatives is equivalent to that of the formalin-fixed specimen.

Dr. Foxall summarized his findings by saying "Anatomy professors and pathologists interviewed agreed that the alternative specimens were less noxious, had good color and texture, and were easier to dissect. Gross preservation was very good and would serve as excellent educational tools to demonstrate anatomy. The alternatives provide for a better and safer laboratory environment with less potential hazard, less odor and less protection needed."

While virtual/video dissection experiences have no detectable odor or special chemical handling and their longevity should be comparable to formalin, many experts have the opinion that watching a video is not the same as, and does not substitute for, hands-on dissection of specimens in a laboratory class. However, the educational utility of video and/or virtual dissection may vary with the class or instructor. Such on-line or video tools (see for example the virtual pig dissection at http://www.whitman.edu/biology/vpd/main.html) may, however, be a useful adjunct to actual dissection. Several sites are free and videos are inexpensive[5]. Virtual, video and CD-ROM software programs also potentially expand the learning opportunity to include study of human anatomy. CD-ROM based programs such as Bodyworks and A.D.A.M. are very well produced, comprehensive, interactive, colorful and provide a very good human anatomy learning experience for even very young children. Although these software packages can be expensive, they are a one-time cost to a school. They may be used as a complete lesson or in addition to actual animal dissections.

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[5] $30 at http://www.educationalimages.com/it030022.htm

Financial Assessment

The prices of alternative specimens were similar to each other and generally less expensive than the formalin-fixed frog from NASCO. Formalin-fixed specimens that are also shipped in formalin without washing may be less expensive, but Dr. Foxall did not believe that educators were likely to purchase such specimens. All companies offered bulk discounts. Regulatory costs associated with formaldehyde use are avoided.

Table 4.4.2 A: Specimen Costs

Grass Frogs	Cost Each in a Package of 10
Formalternate	$2.85
Ward's	$4.10
S.T.F.	$3.63
NASCO Formalin-Fixed, Washed and Propylene Glycol Shipped	$5.60

Human Health and Safety Assessment

Educational specimens themselves contain very little preservative chemical when shipped—no more than a few percent of the specimen is preservative. Handling and dissecting specimens potentially exposes students and instructors to skin and inhalation hazards. The exposures are likely to be short in duration on any given day, but extend over a period of weeks. For instructors, these exposures occur with the teaching of every class. None of the alternatives contain ingredients known to be carcinogens or to cause long-term or reproductive health effects. However, all of them have some potential for skin irritation and some have potential to sensitize after repeated exposure, leading to allergic skin reactions and sometimes asthma. Both Formalternate and S.T.F. are chemical mixtures making evaluation of their potential impact more complicated. For example, Formalternate contains propylene glycol which, by itself, has very low toxicity. However, it may enhance skin penetration of other chemicals.

Flinn's Formalternate is a proprietary mixture of propylene glycol, ethylene glycol phenyl ether, and phenol in undisclosed proportions. Propylene glycol can be assumed to be the main ingredient by the MSDS's description of Formalternate as a "propylene glycol-based formaldehyde substitute." Propylene glycol—a main component of anti-freeze and de-icing solutions—is accepted by the Food and Drug Administration as a food, cosmetic and drug additive and is considered "generally recognized as safe." It has an extremely low vapor pressure and is unlikely to get into the air to be inhaled. In a very few people, especially those with underlying conditions, it may cause skin irritation, hives or an allergic contact dermatitis. It will cause eye irritation if placed directly in the eye.

Ethylene glycol phenyl ether, also known as 2-phenoxyethanol, has an even lower vapor pressure and lower potential for inhalation. It is not readily adsorbed through the skin, although it may cause some irritation.

Phenol is toxic and highly corrosive to the skin. Since it has a low vapor pressure but is absorbed by the skin, the skin is the most likely route of exposure. Phenol is an EPA-registered pesticide and animal studies have shown high acute oral toxicity (USEPA 2006). Its male rat LD50 is 317 mg/kg (compared to formaldehyde's 100 mg/kg). There are no known potential long-term or reproductive health effects of the chemical ingredients in Flinn's Formalternate.

Ward's frogs are preserved with glutaraldehyde with the MSDS reporting that the frog contains less than 1% glutaraldehyde. Glutaraldehyde is a strong irritant and a sensitizer. Acute health reactions including irritation, nausea, headaches and nosebleeds, and allergic reactions including asthma are have occurred in workers in healthcare settings where glutaraldehyde is a common disinfectant (and registered as such by EPA)(NIOSH 2001). OSHA does not have a PEL for glutaraldehyde although it has proposed a limit of 0.2 ppm which is the California OSH PEL for an eight-hour exposure (this compares to the 0.75 ppm OSHA standard for formaldehyde.) ACGIH has a ceiling TLV of 0.05 ppm (15 min maximum exposure) for glutaraldehyde which is approximately the odor threshold. This compares to the formaldehyde OSHA ceiling limit of 2 ppm. Glutaraldehyde becomes irritating at about 0.3 ppm whereas formaldehyde can irritate at 0.1 ppm although these are subjective values. Acute toxicity values reported for glutaraldehyde vary widely, with oral-rat LD50 values varying from 134 mg/kg to 820 mg/kg, carrying a determination of moderately to slightly toxic. The EPA is currently reviewing glutaraldehyde in order to determine its eligibility for re-registration and will most likely publish consensus values in this process. In summary, glutaraldehyde has many of the same hazards as formaldehyde although it has not been judged a carcinogen by any agency. Glutaraldehyde is a liquid at room temperature with a fairly low vapor pressure of 17 mm Hg (at 68° F). Thus, a 1% solution of glutaraldehyde is likely to result in a lower air concentration than the formaldehyde concentration released from an equivalent amount of formalin.

Nebraska Scientific's S.T.F. or Streck Tissue Fixative is composed of diazolidinyl urea; 2-Bromo-2-nitropropane-1, 3-diol (Bronopol); zinc sulfate and sodium citrate. Percentages are only given for Bronopol (less than 3%) and zinc sulfate (less than 2%). This mixture is slightly acidic and therefore potentially irritating to the skin, eyes and respiratory system, but is not likely to be inhaled based on the low vapor pressures of constituents. All of the ingredients are irritants.

Diazolidinyl urea and Bronopol have been found to be skin sensitizers in patch testing studies and case reports, although sensitization is rare. In a study of 8,149 patients in European dermatology practices, 0.5% of patients had allergic reactions to Bronopol (Frosch et al. 1990). The male rat LD50 is 307 mg/kg (compared to formaldehyde's 100 mg/kg). Diazolidinyl urea is a "formaldehyde-releaser" in aqueous solutions. An aqueous product containing 0.5% diazolidinyl urea (the US and European standard for cosmetics), will thus contain and potentially release 0.215% free formaldehyde (Scientific Committee on Cosmetic Products and non-Food Products Intended for Consumers 2002). There is no information about the long-term effects of exposure to diazolidinyl urea, zinc sulfate and sodium citrate, but all are FDA-approved for use in cosmetics, drugs and food. Zinc sulfate was once an EPA-registered pesticide, but is no longer used in pesticide products on the market.

Like formaldehyde, many of the chemicals used in alternative preservatives are irritating to the skin, eyes and respiratory tract, and some may be sensitizers. Phenol may penetrate latex gloves, but this is not likely given the limited contact time and the low concentration of the chemical in the specimens. The alternatives do not have other known long-term health effects or reproductive health effects. Additionally, none of the alternatives contains chemicals that are especially volatile, thus the potential for exposure through the inhalation route is low.

Environmental Assessment

Like formaldehyde, phenol is classified under the Clean Air Act as a "hazardous air pollutant," but unlike formaldehyde, which is a gas at normal temperatures, pure phenol is a solid at room temperature with a low vapor pressure. Phenol is also acutely toxic to fish and several other species. Zinc compounds are also toxic to fish. Phenol, bronopol, and glutaraldehyde are EPA-registered pesticides and therefore toxic to some organisms. Neither formaldehyde nor any of the alternatives are likely to persist or bioaccumulate. Specimens preserved in these alternatives can be disposed of with regular waste.

Summary

All of the alternatives assessed here, with the exception of video/virtual dissection, match or exceed the important technical and performance criteria for educational specimens. Additionally, while the alternatives contain chemicals that can irritate the skin, eyes and respiratory system, they are less likely to do so than formalin-preserved specimens. The alternatives contain ingredients that have been found in some people to be sensitizers, with gluteraldehyde the most likely of the chemicals to cause dermatitis and asthma. The alternatives do not contain any chemicals known to have long-term or reproductive health problems and are not classified as carcinogens as is formaldehyde. However, S.T.F. includes a formaldehyde-releasing chemical. Specimens preserved with this fixative may, in fact, release some formaldehyde. Additional studies may be required to determine the long-term effects of exposure to these alternative chemicals.

Formaldehyde must be disposed of as hazardous waste and formalin-preserved specimens may require special waste handling, but the alternatives and specimens preserved in them do not. Some of the chemicals used in the alternative fixatives are more toxic to fish and other species than is formaldehyde. In general, the low volatility and small amounts of preservative in the alternative specimens suggests that exposure to humans and the environment are likely to be very low. Life cycle considerations for the alternatives include the use and disposal of some ingredients, such as phenol and zinc sulfate that are potential environmental pollutants. Table 4.4.2 B summarizes the findings of this assessment.

Table 4.4.2 B: Assessment Summary for Preserved Specimens for Educational Dissection

Assessment Criteria		**Formalin-Fixed Specimen (Reference)**	**Comparison Relative to Specimens in Formalin**			
			Form-alternate (propylene glycol based)	**STF** (includes Diazolidinyl urea)	**Ward's** (glutaraldehyde based)	**Video/ Virtual Dissection**
Technical/Performance Criteria	Color	Not life-like	+	+	+	n/a
	Texture	Hardened	+	+	=	n/a
	Stiffness	Rigid	+	+	=	n/a
	Odor	Irritating	+	+	=	+
	Longevity	Indefinite	?	?	-	+
	Special handling	Extensive	+	+	+	+
	Availability	Good	=	=	=	=
	Educational value	Good	=	=	=	-
Financial Criteria	Cost (per specimen)	$5.60	+	+	+	n/a
Environmental Criteria	EcoToxicity	Not acutely toxic, except to zooplakton	-	-	-	+
	Hazardous Waste Storage/ Disposal	Regulated	+	+	+	+
	Carcinogen	Yes	+	+	+	+
Human Health Criteria	LD50 (oral rat)	100 mg/kg	+	+	+	+
	Sensitizer	Yes	+	+	=/+	+
	Skin Adsorption	Yes	=	=	=	+
	Irritation	Severe	+	+	+	+

Comparison Key + Better = Similar - Worse ? Unknown

4.4.3 Alternatives Assessment for Hardwood Plywood and Structural Use Building Panels

The choice of building materials by architects, engineers, specifiers, and builders is based on many different criteria: the expected performance of materials, client demands, codes and standards, site specific concerns, project constraints, marketing opportunities, available supply, current and costs and many intangibles such as aesthetic appeal and familiarity. The assessment presented here is a product of the Institute's interviews with product manufacturers, marketers and users; input from stakeholders; and evaluations by outside experts.

Technical Assessment

Different technical criteria apply to building panels depending upon the specific application. For example, exterior panels need to be able to withstand the elements during construction and over time. Interior panels used for high-end applications need to look good and many need to tolerate kitchen and bathroom moisture. Non-structural panels do not need to meet mechanical requirements related to bearing loads. Because of these varying technical criteria, the alternatives are evaluated below in groups:

1. Hardwood plywood
    - traditional hardwood veneer core plywood with formaldehyde-based adhesive (baseline)
    - hardwood plywood with PureBond soy-based adhesive
2. Structural use building panels
    - OSB/softwood plywood using formaldehyde-based adhesive (baseline)
    - Homasote recycled paper-based panels
    - Viroc wood fiber-Portland cement panels
3. A separate discussion of JER Envirotech plastic-wood composite panel board as a potential "near-horizon" particleboard alternative is also included.

Hardwood veneer core plywood

Columbia Forest Products began producing PureBond no-added formaldehyde hardwood plywood with a no-added formaldehyde veneer core in 2005. The design of the proprietary soy-based resin used in the PureBond products is based upon the work of Dr. Kaichang Li at Oregon State Universities' School of Forestry and has been commercialized by Hercules Incorporated (Liu, Li 2002). Soy resins have failed in the past because they lacked strength in the presence of moisture and degraded with time. Dr. Li combined soy proteins with a nylon polymer manufactured by Hercules, Inc. *i.e.*, Kymene® 624 Wet Strength Resin, a product based upon polyamide-epichlorohydrin (PAE). Kymene is typically used by the paper industry to impart wet-strength to paper products such as tissues and towels. (Hercules is marketing this product as ChemVisions™ CA1000 for application in wood products.)

Columbia has further developed the application of this resin to the manufacture of wood panels. This has involved an extensive research and development effort including substantial capital investment in new equipment and processes. Columbia is in the process of converting all of its operations, including the manufacture of flooring, plywood, particleboard, MDF, and agrifiber board, to the use of this new resin. Currently, only the hardwood veneer core plywood is available, but they expect the flooring products to be available soon. (They report that they have succeeded in producing particleboard with PureBond, as well, and will be contracting with a particleboard plant to begin commercial production soon.) Columbia is the largest manufacturer of hardwood plywood in North America.

According to the Hardwood Panel and Veneer Association, the principal performance criteria and characteristics for hardwood panels are: appearance characteristics per wood species, such as number of knots and burls; panel construction; fire resistance; core and back grades; glue bond performance; formaldehyde emissions; moisture content; dimensions; and finish of the panel (Hardwood Plywood & Veneer Association (HPVA)). The association has developed its own voluntary standard called the "ANSI/HVPA HP-1" standard that incorporates these criteria.

No independent test results were available for the Purebond product, so the assessment relied on the manufacturer's own testing and input from those who had used the product. Appearance characteristics are the most important technical criteria. The adhesive generally does not affect appearance characteristics, so these are considered equal between the PureBond product and the traditional product. (Columbia provides a full comparison of their products with the ANSI on their website at: http://www.columbiaforestproducts.com/products/default.asp.)

The second important characteristic is the glue bond performance. Columbia in-house tests found significantly improved water resistance in comparison to a board made with urea-formaldehyde adhesive. They found that the PureBond board performs as well as type II urea formaldehyde adhesive construction in hardwood plywood as defined by ANSI/HPVA HP-1-2004 standards. These standards require manufacturers to conduct three-cycle boil and three-cycle soak tests. Ninety percent of PureBond panels passed the boil test (vs. 0% of traditional urea-formaldehyde bonded panels) and 100% passed the soak test. Because PureBond panels do not pass the boil test 100% of the time, Columbia's panels are not rated as structural or exterior-grade.

A third important characteristic is the fire resistance of the product. The standard for fire resistance is the ASTM-E-84 test which rates products by a flame spread index. The test determines the distance and the rate of travel of flame in ten minutes. Columbia reports that its PureBond product rates within the requirements for Class C Flame spread index of 76-200. The HPVA reports the flame spread of other veneer core plywood panels as between 114-173 (American Forest & Paper Association, Inc. 2002). Generally, products that have a flame spread index of less than 200 will meet all building code requirements for interior applications.

An outside expert, Mark Kalin, received feedback that a woodworking firm that had found that the PureBond panel did not lay flat. Columbia's response was that the PureBond panel is as flat as any veneer core hardwood plywood panel and that they have not had returns or complaints. According to the Architectural Woodwork Institute, the veneer core panel type rates "fair" in comparison with alternatives like particleboard and MDF panel types that are rated as "excellent" for flatness (American Woodworking Institute (AWI) 2003). Veneer core panels may buckle with climate-related temperature and humidity changes and the PureBond product is no different from others in this respect, according to a product supplier (Laing 2006). Paul Quimby of Neil Kelly Cabinets of Portland, Oregon uses PureBond for a small amount of their business and has not had problems with the product. Columbia's PureBond products are available in Massachusetts from Atlantic Plywood Supply in Woburn. They have had no customer complaints about the product. They also anticipate a significant market for no-added formaldehyde products.

While the resin chemistry is not exclusive to Columbia Wood Products, other manufacturers who want to use it will have to invest significant process development and redesign resources, as Columbia has done.

Structural Use Panels

Homasote's recycled paper panels and Viroc's wood-Portland cement panels may be used in place of softwood plywood and OSB in exterior sheathing, roof decking and floor decking. Homasote has been made in New Jersey since 1909 and is primarily marketed as an acoustical barrier (see www.homasote.com). Homasote also makes a product (ComfortBase) that may be used in place of plywood as a carpet or tile underlayment over concrete and one that may be used in place of plywood for concrete forming. Due to time limitations, those uses could not be evaluated. Viroc is made in Portugal and represented and distributed in the US by Allied Building Supply (see www.viroc.pt and www.alliedbuilding.com). The company began producing the product in 1994 and it is used extensively in Europe.

Technical and performance criteria for these uses relate to strength, weight, how they handle moisture, storage, handling, fastening, finishing, fire resistance, thermal resistance, and mold, rot and insect resistance. (Some of the values for these criteria are shown in Table 4.4.3 A) The APA (the Engineered Wood Association formerly known as the American Plywood Association) has developed a rating and grading scale for plywood and OSB that manufacturers use to mark their products according to the accepted use. Panels are given one of four "exposure durability" ratings: Exterior, Exposure 1, Exposure 2 and Interior (the U.S.'s sister organization in Canada uses a similar Can-Ply rating system). This rating system is based upon the strength of the glue bond, as weather will delaminate the boards and cause them to deteriorate. Only member mills can use these ratings and markings, thus imported products and non-wood panels will not be APA-rated. Because Homasote and Viroc are not members of the APA and do not use glue, they are not APA-rated.

The strength of a panel is measured in several ways and is a very complex phenomenon. ASTM has standardized tests for panels for shear strength, compressive strength, impact resistance, wind resistance and tensile strength. Additionally, structural panels have span ratings that reflect both the load that can be carried and the stiffness of the board. Panels used for roof and floor decking must meet building codes designed to prevent collapse. The span rating or load value is how much load a panel can take when fastened to joists at various distances from each other. The span rating can be increased by using thicker panels, but that will increase the weight of the panel. One reason why wood panels are so popular is their excellent strength to weight ratio.

Homasote's floor deck product is sold in either 1-11/32 in. thick panels for 16 in. spans or 1-3/4 in. thick panels for 24 in. spans and is designed to withstand live loads of 100 lb/in^2. The latter material weighs 4.1 lb/ft^2 compared to about 2.3 lb/ft^2 for a similarly span rated ¾ in. plywood or OSB panel. Viroc will bear a 100 lb/in^2 load with 24 in. span in the 7/8 in. thickness and weighs 5.7 lb/ft^2. Thus, relative to plywood or OSB, Homasote and Viroc both must be thicker and heavier, to carry the same load.

Dimensional stability, or the ability of a material to retain its shape when exposed to changes in temperature or moisture, is an important characteristic of a structural board. Changes in dimensional stability can affect the structural integrity of the board and therefore the building. Moisture induced buckling may persist even after a board has dried out. There are several tests that assess factors related to dimensional stability and the results of which may predict the success of a product in an exterior application. Linear expansion is evaluated with ASTM D1037 and is how much the panel will grow when exposed to a change in humidity. Like plywood and OSB, Viroc and Homasote will absorb and desorb moisture according to the climate, and therefore potentially grow or shrink. Both companies stress the need to condition the products at the site prior to use.

In plywood and OSB, significant expansion and shrinkage will wear the glue bonds; its impact on differently bound panels is difficult to predict. Viroc has a slightly better value for this metric, while Homasote does not perform as well as plywood or OSB. In addition, how quickly and thoroughly a panel dries out or "wicks" moisture is also important, but there are no standardized tests for wicking ability. While exterior sheathing is not designed to be constantly exposed to the elements, water may get under cladding or siding and so an overall assessment of weatherability is important and will be discussed below. In additional to the structural integrity of the panel, moisture may lead to mold problems.

Permeance is a measure of the ability of a material to retard the diffusion of water vapor, which is measured in ASTM test E-96 in units called "perms." Traditional softwood plywood and OSB are classified as "semi-vapor permeable" or vapor-retarders (Lstiburek 2002). In cold climates, it is better to have a more permeable exterior sheathing because buildings will dry from the inside out. Less permeable exterior sheathing may trap moisture leading to mold problems. Homasote and Viroc have greater permeance results than plywood and OSB.

A very important criterion is the structural integrity of the product over time given exposure to actual conditions, with the most important condition being moisture. Unfortunately, there are no standards or ASTM tests for "weatherability" outside of the APA's rating system which is based on glue bond integrity. Because Homasote is made of recycled paper, architects and others have assumed that it will fall apart when exposed to moisture. The company claims that it will dry out and maintain its structural integrity (see http://www.homasote.com/about.html). Homasote is reportedly a very good "wicker" (there are no standard values for this) and when place in a vertical plane, moisture will run to the bottom of the panel via gravity. In a horizontal plane when exposed to moisture, it is likely not to hold up. However, plywood and OSB will also delaminate under such conditions.

Homasote was used extensively in exterior applications from the 1930's until the 1980's when OSB became the less expensive alternative to plywood. (With the increasing cost of OSB, the manufacturer notes increased sales of Homasote for exterior applications.) Homasote's website has pictures of a demonstration of weatherability that show it holding up to the elements as experienced in New Jersey. Consisting of 80% Portland Cement, Viroc's weatherability is reported to be excellent. Despite the importance of this technical criterion, until there are long-term standardized tests of weatherability, it is not possible to definitively compare these products on this measure.

While Homasote and some plywood and OSB panels are treated with borate to improve insect and fire resistance, Viroc is not combustible and will not be attacked by termites, mold or other organisms. Homasote has the same fire rating as plywood and OSB (Class C), but like other composite products, it can be treated with fire retardants to become a Class A product (N.C.F.R. Homasote). Homasote claims that its panels are not very attractive to insects. Viroc reports independently conducted tests of its impact and wind resistance and claims these qualities as a particular benefit of the product (ICC Evaluation Services, Inc. 2003). Viroc is being used to construct temporary school units in Florida and was specified because of its expected durability in the face of Florida's complement of termites, mold, moisture, and hurricanes. Homasote gives a "Janka ball" hardness test result of 230 lb, meaning that only 230 lb of force are required to imbed a 0.444 in. steel ball halfway into the material. This compares with a 660 rating for soft Douglas fir.

Product handling is very important and the principal concerns are weight, storage conditions, cutting, fastening and finishing. These factors differ between plywood/OSB and Homasote and Viroc. Viroc is considerably heavier than the other products. Homasote is lighter in the equivalent thicknesses, but as was mentioned earlier, may need to be thicker and therefore, heavier, to withstand the same loads.

All of the panels, including plywood and OSB, need to be stored and handled in such a way as to prevent warping, contact with moisture, and impact by forklifts – generally covered with tarps on pallets. All would need to dry out prior to being "sealed" in a building under cladding or flooring. Plywood may be more forgiving than the others of rough handling and Viroc stresses the importance of avoiding "breakage." Viroc can be machined like wood, but thicker boards will need to be cut with tungsten carbide tipped saw blade (preferably equipped with vacuum extraction) and pilot holes will need to be first drilled or self-drilling ("grabber") screws need to be used. It may be difficult to use nails with Viroc. It is likely to wear out bits and blades at a quicker rate than the others.

Ringshank nails or drywall screws can be used with Homasote, but the company specifies that distance between nails be 3 in. or 6 in. depending on the span and location of the panel. It may be easier to nail Homasote, but more nailing is required—plywood and OSB need fasteners 6 in. or 12 in. apart for sheathing and subfloors. Homasote is easy to cut with a saw and can be cut with a mat knife depending upon the thickness. Nails in Homasote and Viroc are much more secure than in plywood or OSB according to results of ASTM dry "nail pull" tests. Both Viroc and Homasote can be finished with latex paint. The unpainted surfaces of both are a dull gray with some texture.

The "R" factor, or thermal resistance factor, of Homasote is twice that of plywood and OSB making it a better insulator. Viroc's R factor is considerably lower than plywood and OSB.

Both Homasote and Viroc are available in Massachusetts. Viroc is distributed in the U.S. by Allied Building Supply (www.alliedbuilding.com); their supplier in Massachusetts is United Builders Supply (40 Waverly St, Framingham, MA (508) 879-1000). Homasote is available through Home Depot and dozens of other building products suppliers in Massachusetts.

Table 4.4.3 A: Performance Values for Structural Use Panels

	Softwood Plywood	**OSB**	**Homasote**	**Viroc**
Weight (1/2 in.) lb/ft^2	1.6	1.7	1.2 (heavier at equivalent span rating)	3.1
Tensile Strength lb/in^2	1,500-4,000	1,000-1,500	450-700	793
Shear	165 lb/ft	175 lb/ft	225 (field)	n/a
Permeance	.8	.8	12	2.7
Linear Expansion (50-90% RH)	.15	.15	0.25%	0.14%
Nail Pull (Dry)	50 lbs	40 lbs	125	325
R Value	.6	.6	1.2	0.36

Human Health and Safety Assessment

Columbia's Purebond veneer core panel is made with hardwood species wood glued together with soy flour "blended with a very small amount of proprietary resin," according to Columbia's website. That resin is Hercules Inc. chemical Kymene® 624 Wet Strength Resin, now called ChemVisions™ CA1000, a liquid cationic amine polymer-epichlorohydrin amine called polyamide-epichlorohydrin (PAE). Neither the PureBond MSDS nor the Kymene® 624 MSDS notes the inclusion of any hazardous ingredients. The Kymene® 624 MSDS warns that repeated contact with the resin may cause skin, eye and respiratory tract irritation and skin sensitization in "susceptible" individuals resulting in dermatitis. Columbia reports that the addition to and mixing of the PAE with the soy flour is a closed process and manufacturing workers do not have contact with the PAE or the mixed PAE-soy resin.

Although life cycle considerations are limited within the scope of this report, it is important to consider that the PAE chemical is manufactured with epichlorohydrin, a probable human and confirmed animal carcinogen. Epichlorohydrin is also acutely toxic to humans and overexposure can cause severe damage to the liver, kidneys, eyes and respiratory tract (Hazardous Substances Data Bank). It is also a skin and respiratory sensitizer, causing asthma and dermatitis. It is mutagenic and may cause infertility in men. According to the manufacturer and the EPA, epichlorohydrin is completely consumed in the batch manufacturing process used to make the resin. There are no emissions from this process and no residual or "free" epichlorohydrin in PAE where it is irreversibly transformed in the polymer matrix (Steib 2006; USEPA 1984). Because of this, there is apparently no potential for worker, consumer or environmental exposure to epichlorohydrin during PureBond building panel manufacture, use or disposal.

Those employed in the manufacture of epichlorohydrin are likely to have to greatest potential for exposure, followed by those exposed in the Kymene manufacturing process. NIOSH conducted industry wide surveys of epichlorohydrin exposures in five facilities in the 1970's. Three of these were plants that manufactured kymene resins, including a Hercules plant in Georgia. In that survey, the two sampled production workers were exposed well below the PEL of 5 ppm and also well below the ACGIH TLV® of 0.5 ppm. Their time weighted average exposures were 0.15 and 0.05 ppm (Bales 1978). Epichlorohydrin has a vapor pressure similar to water and can be absorbed through the skin.

Soy flour is not known to have any negative health effects. Wood dust can cause skin and respiratory tract irritation and even sensitization. Additionally, both IARC and the EPA's NTP program have designated wood dust as a carcinogen with hardwood dust, specifically, associated with adenocarcinoma of the nasal cavities and paranasal sinuses (Hazardous Substances Data Bank).

Like PureBond, Viroc and Homasote do not present a health and safety or environmental hazard to building occupants. Since they are not bound with a resin, per se, the health and safety issues they present relate to the substrate itself. Considerable dust may be generated in cutting Viroc and Homasote. Viroc recommends that vacuum fitted cutting tools and dust masks be used. The dust generated would be composed of wood dust and Portland cement dust both of which present potential hazards. As mentioned above, wood dust is a potential carcinogen and a respiratory irritant. Cement dust may contain free silica.

Homasote dust is recycled newspaper (cellulose). Studies of paper and pulp workers have found exposure-related chronic bronchitis and excess cancers, but these mills workers were exposed to many chemicals in addition to cellulose. Exposure to cellulose dust and fibers was found to cause reversible respiratory tract inflammation in rats, and cellulose dust is thought to be of low toxicity, despite the durability of cellulose fibers in the lung (Cullen et al. 2000). Pulmonary and intraperitoneal inflammation induced by cellulose fibres.)

Portland cement is made of calcium compounds including tri and dicalcium silicate, tricalcium aluminate, tetracalcium aluminoferrite, and gypsum (calcium sulfate dihydrate). Due to its alkalinity, Portland cement can be irritating to the respiratory tract, skin and eyes. Trace contaminants of hazardous metals and minerals may be present in Portland cement including free crystalline silica, chromium, nickel, calcium and magnesium oxide, potassium and sodium sulfate. Crystalline silica is a human carcinogen according to EPA's NTP program and IARC. The trace amounts of chromium in Portland cement are thought to contribute to allergic contact dermatitis in a small percentage of exposed workers, although such skin problems may also be due to repeated exposure to the drying effects of prolonged skin contact with wet cement (Sahai 2001).

European Union Directive 2003/53/EC limits the amount of chromium IV in Portland Cement to 0.0002% or 2 ppm due to its sensitizing properties. This is being done through selection of raw materials less likely to contain trace chromium and by the addition of reducing agents. Both the OSHA standard and the ACGIH TLV for Portland Cement are set at 10 mg/m^3 (compared to 0.5 mg/m^3 for lead, for example).

Potential manual material handling hazards are significant for Viroc due to its greater density. Company materials address this concern and recommend that panels be lifted and carried by two or more people and that trollies and other devices be used to transport panels.

Environmental Assessment

The PureBond hardwood plywood board is not expected to have any environmental impact beyond those of traditional boards. (Customers may specify PureBond veneer core hardwood panel certified sustainable by the Forest Stewardship Council). Soy flour has no known environmental impact. The Kymene resin, itself, is acidic (pH 2.6-3) and therefore toxic to several aquatic species. Safe disposal of the resin requires pH neutralization. It does not readily biodegrade. Epichlorohydrin is a hazardous air pollutant, a regulated water pollutant, and must be treated as hazardous waste. It will volatilize from soil and water and has a half life of 36 days in air. It does not bioaccumulate.

Epichlorohydrin is not a potential environmental release from the panel manufacturing process. It is released from Hercules manufacturing facilities, however. According to TRI data, Hercules reported over 19,500 pounds of epichlorohydrin environmental releases in 2002 (combining all facilities' releases), almost all of these were releases to air (Green Media Toolshed, Inc.). The amount of these releases attributable to the manufacture of the PAE resin for the production of PureBond is not known, but is likely to be very small considering that the main use of PAE is in paper manufacture and that Hercules uses epichlorohydrin to make other chemicals. Nevertheless, a dramatic increase in the use of PAE resin for the production of wood products could result in increases in epichlorohydrin environmental releases.

Neither Homasote nor Viroc (nor their constituents cellulose and Portland Cement) are expected to have any negative impact on the environment from a toxicity standpoint. From a resource conservation standpoint, Viroc is only 20% wood and can be made with waste wood thus avoiding harvest of virgin forests. However, Portland cement must be mined and therefore is not a renewable resource. Homasote not only does not use any virgin wood, it is at least 80% post-consumer recycled materials that otherwise would be headed for landfills or incinerators. Homasote touts its environmental performance as follows:

> Each year Homasote building products help conserve more than 1,370,000 trees and eliminate more than 100,000,000 pounds of solid waste each year. Each production day up to 300 tons of post-consumer paper are recycled into Homasote, diverted from waste stream disposal into landfills or other methods. All water used to manufacture Homasote® products — hundreds of thousands of gallons per day — is completely recycled in a "closed loop" system.

From an energy use standpoint, Viroc has several concerns. The making of Portland Cement in one of the world's most energy intensive industrial activities resulting significant greenhouse gas, dioxin,

NO_x, SO_2, and particulates emissions. For every ton of Portland cement produced, one ton of carbon dioxide is released to the atmosphere (Portland Cement Association). Additionally, significant amounts of fossil fuels are consumed in the production of Viroc as the Portland Cement and wood fibers are transported to Portugal and then back to the United States and then around the country. Building Green Inc., publishers of Environmental Building News, have not given Viroc its imprimatur as a "green" product because of this extreme energy intensivity.

Financial Assessment

Veneer core hardwood plywood is a high quality, high cost product. Columbia PureBond product costs the same as the traditional product produced with urea-formaldehyde resin (approximately \$1.25/ft^2.)

Homasote's sheathing panels are more expensive at \$15-25 for ½ in. 4x8 panel, than OSB (\$13) and plywood (\$14), but costs are within reach, especially if OSB mill problems arise. Homasote's floor decking is much more expensive than traditional alternatives.

At \$96 for a ½ in. 4x8 panel, Viroc is more than seven times the cost of OSB and plywood, but offers qualities such as fire, wind, impact and insect and mold resistance that may make it attractive to certain markets nonetheless. Viroc can be used without cladding, thus saving some portion of the additional expense.

Near Horizon Alternative: JER Envirotech plastic-wood composite panel

In British Columbia and in Malaysia, with support from the Canadian government, the JER Envirotech company is in process of developing an extruded building panel made of wood fiber and polypropylene thermoplastic (JER Envirotech Ltd.). They expect to begin selling these panels in the US in the next year. Currently, they view this product as a substitute for particleboard and not a structural product although they will be submitting it to a testing protocol and ultimately expect it to perform as a structural product. Wood-plastic composite products are used extensively in this country as substitutes for wood lumber, but JER Envirotech will be the first to produce a panel from this material. Their website describes the JER panel as superior to plywood due to its superior high temperature heat deflection, superior fire resistance, resistance to biological degradation (*e.g.,* insects, decay, termite etc.), very low water absorption, superior mechanical properties (tensile, flexural, and impact resistance), resistance to thermal degradation and its lack of formaldehyde. They also suggest that the price will be competitive. Polypropylene thermoplastic does not have recognized health and environmental effects except for a potential for respiratory irritation from exposure to polypropylene fumes during manufacture of the raw material (Hazardous Substances Data Bank). Wood dust is recognized as a carcinogen.

Summary

Columbia's PureBond compares well to the traditional product in the technical and financial assessment. While it eliminates potential formaldehyde exposures, it does introduce a new potential hazard, epichlorohydrin, into the lifecycle of building panels. This hazard is unlikely to threaten building occupants or workers exposed to the Kymene resin, but is a potential (although low) worker and environmental hazard in the manufacture of the intermediates.

Viroc and Homasote panels may satisfy enough technical requirements to be considered for structural uses in buildings, especially for those interested in "green" or low toxicity construction. Each has unique advantages and potential disadvantages. Advantages for Homasote include is lack of toxicity and beneficial environmental impact. Additionally, due to its high perm rating and wicking ability, it may prove to be a durable material that helps to prevent mold problems. Viroc has entered the US market at a time when builders in the South and around the country may be looking for hurricane, fire, mold and insect proof building materials that will not negatively impact indoor air quality. Its high cost is likely to prevent it from substituting directly for plywood or OSB, except where these qualities are highly desirable, or where designs utilizing Viroc can eliminate cladding or insulation. Although the Portland cement industry is working to reduce its environmental impact, Viroc's inherent energy intensivity will not appeal to green builders and customers with lifecycle perspectives.

"Green" building products are developing at a rapid pace. Concerns with resource and energy conservation and indoor air quality for building occupants has driven the development of programs such as the U.S. Green Building Council's LEED certification program. These types of initiatives have fostered innovation in new materials development and a market for greener construction materials. Additionally, traditional product suppliers may begin producing plywood and composite wood products made with soy-based (or other) resins and plastic-wood. If the demand for no-added formaldehyde products increases, plywood makers may use more polyvinyl acetate glue in their existing presses despite the increased cost and production challenges. In the meantime, in addition to the "no added formaldehyde" products evaluated here, use of wood products made with low-emission formaldehyde resins will continue to reduce exposures to formaldehyde.

Table 4.4.3 B: Assessment Summary for Hardwood Plywood Building Panels

Assessment Criteria		**Traditional Formaldehyde-based Resin Plywood (Reference)**	**Comparison Relative to traditional formaldehyde resin Plywood**
			PureBond soy-based adhesive
Technical/ Performance Criteria	Appearance/ Construction	ANSI/HVPA HP-1-2004	=
	Glue bond under moisture	Good (ANSI 3-cycle soak)	=
		Poor (ANSI 3-cycle boil)	+
	Fire Resistance	Good (ASTM E-85 Flame Spread Class C)	=
	Warp Resistance	Variable	=/?
	Product Availability	Good	=
Financial Criteria	Cost (1/2 in. 4x8)	$1.25/ft^2 (Columbia's price)	=
Environmental Criteria	Ecotoxicity	Minor	=
Human Health Criteria	Carcinogen in Resin	Yes	+
	Toxic Intermediate in Resin	Yes	=
	Irritant in Resin	Yes	+

Comparison Key + Better = Similar - Worse ? Unknown

Table 4.4.3 C: Assessment Summary for Structural Use Building Panels

Assessment Criteria		Softwood Plywood with formaldehyde-based resin (Reference)	OSB (Oriented Strand Board) (Reference)	Comparison Relative to formaldehyde-based resin Softwood Plywood and OSB	
				Homasote	**Viroc**
Technical/Performance Criteria	Weight (1/2 in.) lb/ft^2	Acceptable	Acceptable	+	-
	Fire Resistance	Good (Class C)	Good (Class C)	=	+
	Insect/Rot/Mold Resistance	Acceptable	Acceptable	+	+
	Load bearing/weight	Good	Good	-	-
	Impact Resistance	Good	Less than plywood	-	+
	Tensile Strength lb/in^2	Excellent	Excellent	-	-
	Shear	Good	Good	+	?
	Permeance	Acceptable	Acceptable	+	+
	Linear Expansion (50-90% RH)	Good	Good	-	+
	"Weatherability"	Acceptable	Acceptable but worse than plywood	?	?
	Nail Pull (Dry)	50 lbs	40 lbs	+	+
	R Value	.6	.6	+	-
Financial Criteria	Cost (1/2 in. 4x8)	$14	$13	-	-
Environmental Criteria	Ecotoxicity	Minor	Minor	+	+
	Natural Resource Conservation	Poor	Better than plywood	+	?
	Energy Intensity	Neutral	Neutral	?	-
Human Health Criteria	Carcinogen in Binder	Yes	Yes	+	+
	Irritant in Binder	Yes	Yes	+	=

Comparison Key + Better = Similar - Worse ? Unknown

4.5. Summary and Conclusions

Formaldehyde, a gas a room temperature, is widely used in industry and is a basic building block for the manufacture of many other chemicals and products. More than half of formaldehyde manufactured is used in the production of resins and adhesives and most of these are used in the manufacture of wood products such as plywood. Most formaldehyde is sold as formalin, a water solution of formaldehyde and some methanol to prevent polymerization. Formaldehyde is highly toxic to bacteria and other pathogens and, thus, it is used as a sterilizer. In addition to manufactured sources, formaldehyde can be a product of combustion.

Exposure to formaldehyde can cause irritation and dermatitis and has been found to cause nasopharyngeal cancer in some occupational groups, including embalmers who use formaldehyde to preserve the deceased. Because formaldehyde is highly reactive, water soluble and readily metabolized by almost all human cells, overexposures tend to do damage at the point of contact, most commonly the eyes and the upper respiratory tract.

Rising concerns about indoor air quality have drawn formaldehyde into the spotlight because of the tendency for formaldehyde-containing building elements and furniture to "off-gas" formaldehyde thereby causing irritation to occupants. In response, manufacturers have improved their processes to reduce the potential for off-gassing and standards have been set to certify products as "low-emitters."

We looked at alternatives to the use of formaldehyde in sanitary storage for barbering and cosmetology, preserved educational specimens for dissection, and building panels. These uses were chosen because of their potential to expose students, workers and the public to formaldehyde emissions.

Sanitary Storage in Barbering and Cosmetology

In salons and cosmetology classrooms in Massachusetts, paraformaldehyde sanitizers known as Steri-Dry tubes are required by the Board of Cosmetology to be placed along with brushes and combs in storage cabinets and drawers to maintain an extra level of protection for customers. However, national best practices experts recommend that paraformaldehyde not be used; that storage cabinets be cleaned and disinfected with standard procedures. Thus, the alternative to this use of formaldehyde is to not use it and to abide by sanitary standards.

A second alternative, the use of UV light cabinets, has potential maintenance concerns and could result in UV light exposure. They also represent a significant initial capital expenditure. They also could be used effectively as an alternative to Steri-Dry, however, eliminating the EH&S concerns associated with exposure to formaldehyde.

Educational Specimens

Students and instructors have been exposed to formaldehyde through the off-gassing of specimens such as fetal pigs and frogs dissected in gross anatomy classes. Several scientific supply companies are offering formaldehyde-free alternative specimens and these are generally less expensive, deemed equivalent or better from a technical standpoint, and are generally less toxic. However, these alternative preservatives do contain ingredients that can be irritating to the skin and should be used with skin protection.

Another viable alternative to formaldehyde-preserved specimens is the use of virtual/video dissection technology, which eliminates any exposure concerns associated with formaldehyde. From a technical standpoint, the use of virtual/video dissection offers certain advantages, but many instructors prefer physical dissection. It may also be a useful adjunct to dissection for classroom instruction.

Building Panels

The Institute identified and assessed acceptable alternatives being used by manufacturers of building panels. Two products, one that is recycled paper board and one that is cement-wood fiber board, are made without the use of formaldehyde-based resins, and are feasible alternatives for many structural panel applications. These alternatives are generally superior to the formaldehyde-based structural panels from an EH&S perspective, but are more expensive. In addition, the cement-wood fiber board uses significant amounts of energy in its manufacture.

In addition to material alternatives made without resins, one company is manufacturing wood panels (currently only veneer core hardwood plywood) with a soy-based resin. Because of the addition of a wet-strength ingredient borrowed from the paper industry, this soy-based resin has equivalent or better technical performance to the traditional product. The cost is also equivalent to the traditional product. While there are not expected to be environmental or health and safety hazards related to the use of this alternative resin, the lifecycle of this chemistry includes an intermediate chemical that is a carcinogen.

Finally, an emerging technology, extruded building panel made of wood fiber and polypropylene thermoplastic, is currently being developed as an alternative decorative wood panel. The Institute was not able to assess this alternative compared to formaldehyde-based building panels, however we encourage further study to determine how this alternative compares from an EH&S, technical and cost perspective

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Chapter 5. Perchloroethylene

Five Chemicals Alternatives Assessment Study

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5.1 Overview – Perchloroethylene

5.1.1 Characteristics of the Chemical

Perchloroethylene, or PCE, is a non-flammable, man-made chlorinated hydrocarbon. The chemical contains two carbon atoms forming a double bond and each carbon has two chlorine atoms attached. The resulting chemical formula is C_2Cl_4 and the structure is represented in Figure 5.1.1 below.

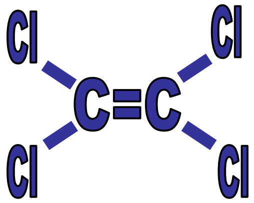

Figure 5.1.1

PCE's Chemical Abstract Series number is 127-18-4. This chemical has many additional synonyms, some of which are ethylene tetrachloride, tetrachloroethylene, perchloroethylene, carbon bichloride, carbon dichloride, perc, 1,1,2,2-tetrachloroethylene, and perchlor.

PCE is produced in the U.S. by three processes: the direct chlorination of ethylene dichloride, the oxychlorination of ethylene dichloride, and the chlorinolysis of hydrocarbons or their partially chlorinated derivatives. In the first two processes, PCE can be produced separately or as a co-product with trichloroethylene (TCE) with the raw material ratios determining the proportions of PCE and TCE. The third produces PCE as a co-product with carbon tetrachloride (Most 1989). Most PCE is produced from ethylene dichloride or other C_2 chlorinated hydrocarbons.

PCE is a clear and colorless liquid with an ether-like odor. It has low solubility in water, 0.015 g in 100 g of water, and has a specific gravity greater than water, 1.62. The vapors from PCE are 5.8 times denser than air, and its vapor pressure is 18 mm Hg at 25° C making PCE heavier than air, which may allow it to collect at toxic levels in poorly ventilated spaces. While PCE is considered to be quite stable, at temperatures greater than 600° F (316° C), PCE breaks down to phosgene, and hydrogen chloride, which are dangerous respiratory irritants (ATSDR 1997). More physical properties are listed in the table 5.1.1 below.

Table 5.1.1: Chemical/Physical Characteristics of PCE
((United States Environmental Protection Agency (USEPA) 1994))

Melting/Boiling Point	-19° C / 121° C
Vapor Pressure	18.47 mm Hg at 25° C
Relative Vapor Density (air = 1)	5.8
Octanol/Water Partition Coefficient	Log Kow = 3.40
Specific Gravity/ Density	1.62 at 20° C 1.6311 g/mL
Solubility	0.015 g in 100 g of water, low solubility in water
Soil Sorption Coefficient	Log Koc = 665
Bioconcentration Factor	39 (rainbow trout, Oncorhynchus mykiss) 49 (bluegill, Lepomis macrochirus)
Henry's Law Coefficient	1.8 x 10-2 atm m^3/mol
Biodegradation (days)	Water 60; Soil 120; Sediment 540; Air 96 (PBT profiler)

5.1.2 Health and Environmental Impacts

Exposure to PCE can be as a result of environmental contamination, presence in consumer products or occupational sources. PCE levels in the environment tend to be higher in urban and industrial areas. The ASTDR estimates that the most prevalent route of exposure to PCE is by inhalation and it is readily absorbed into blood through the lungs.

PCE can be detected by smell at levels ranging from 5 to 50 ppm. Therefore odor is a somewhat adequate detector for acute, high level exposures above the OSHA PEL of 100 ppm. In states that have a lower exposure limit (*e.g.,* California's PEL is 25 ppm), odor would not be an adequate detector. In addition, odor is not adequate for long term chronic exposures, because PCE can dull or desensitize the olfactory senses over a long period of time.

Other exposure routes of concern are oral via drinking water or contaminated food (Habeck 2003). Dermal exposure is generally considered a minor route of exposure but direct skin exposure to PCE in the liquid form can result in irritation and blistering. Target organs for PCE are the central nervous system and the liver (ATSDR 1997). Some studies suggest that frequent over-exposure to some organic solvents over months or years may cause lasting and possibly permanent central nervous system effects. Fatigue, lack of muscle coordination, loss of concentration as well as short term memory loss, and personality changes exhibited as nervousness, anxiety or irritability are some of the potential permanent long-term effects of chronic and frequent exposure (California Department of Health Services 1989). In addition, PCE inhaled by pregnant women can reach a developing fetus and has been found in breast milk of mothers exposed to the chemical (Habeck 2003).

Acute Exposure

For inhalation exposures, PCE can be irritating to the upper respiratory tract, cause giddiness, headache and intoxication. Nausea and vomiting may follow from inhalation of large amounts.

Concentrations of 200 ppm or more have been associated with dizziness, confusion, headache, nausea, and irritation of the eyes and mucous tissue. Exposure to extremely high levels (>1,500 ppm) may lead to unconsciousness due to anesthesia and, in extreme cases, death from respiratory depression. The IDLH for PCE has been set at 150 ppm (NIOSH 1996).

Skin contact with PCE can cause irritation. Symptoms can include redness, itching, and pain. Prolonged exposure can result in the removal of natural protective oils from skin resulting in irritation, dryness, cracking and dermatitis. Likewise, extended dermal contact can result in second- and third-degree chemical burns. Furthermore, contact of PCE vapors above 75 ppm with the eyes will result in irritation, redness, and pain (NIOSH 2000).

Chronic Exposure

Long term exposure to PCE may cause liver, kidney or central nervous system damage. Furthermore, the exposure can yield to an aggravation of pre-existing conditions. For example, persons with pre-existing skin disorders or eye problems or impaired liver or kidney function may be more susceptible to the effects of the substance. PCE can affect your brain and central nervous system as a whole, in a similar way as consumption of alcohol. Therefore the consumption of alcoholic beverages within a short time period of exposure to PCE enhances the toxic effects from PCE and alcohol. The two would have an additive effect on the central nervous system (California Department of Health Services 1989).

Overexposure may result in cumulative liver and central nervous system (CNS) damage or narcosis. Over all, PCE can affect the liver, kidneys, eyes, skin, respiratory system, and CNS.

Reproductive and Developmental Effects

There are conflicting data on the status as PCE as a reproductive and developmental toxin in both humans and animals. Some studies have reported adverse reproductive effects of PCE , including spontaneous abortions, menstrual disorders, altered sperm structure and reduced fertility, but the studies were limited and not conclusive (USEPA 1994).

Studies also have been conflicting regarding birth defects in animals, with some finding increased incidences in liver tumors and leukemia while others find no teratogenic effects. What is widely agreed upon is that PCE is able to transport across the placenta to the fetuses of pregnant women who have been highly exposed. In addition, PCE has been found in the breast milk of nursing mothers.

Carcinogenic Classification

Several agencies have investigated PCE's association with cancer. The National Toxicology Program NTP classifies PCE as "Reasonably anticipated to be human carcinogen" (National Toxicology Program 2005). IARC lists PCE as Group 2A, "Probably carcinogenic to humans." EPA specifies it as "Group B/C, probable/possible human carcinogen" (OSHA 2005) and ACGIH designates it as an A3, confirmed animal carcinogen (ACGIH 2006).

A recent Massachusetts-based research project from Cape Cod involved looking at PCE exposure through contaminated drinking water and found an association between PCE exposure and cancer rates (Aschengrau, et. al, 2003).

Table 5.1.2 summarizes the acute, chronic and cancer hazards associated with PCE.

Table 5.1.2: Perchloroethylene
Acute, Chronic and Cancer Hazards

Acute Effects (Short Term)	**Chronic Effects** (Long Term)	**Cancer Hazards**
• Single exposures can cause CNS effects such as dizziness, headache, sleepiness, confusion, nausea, difficulty speaking and walking. • High- level exposure may cause vomiting, unconsciousness & death • Not considered a significant skin irritant but prolonged exposure with undiluted liquid may cause skin irritation. • An eye irritant causing pain, redness and general inflammation.	• Long-term exposure may cause liver and kidney damage. • Prolonged and repeated exposure may cause dermatitis. • Increased health risks for people with pre-existing skin disorders and impaired renal or liver function.	• Reasonably anticipated to be a human carcinogen, sufficient evidence in animals, by NTP Animal testing has linked high exposure to liver and kidney cancer as well as leukemia. • NIOSH recommends handling it as a possible carcinogen

Worker Health

The OSHA PELs for PCE are 100 ppm for an 8 hour day and a maximum exposure level of 200 ppm for 5 minutes in any 3-hour period. California's state OSHA program has set the PCE permissible exposure level at 25 ppm, 75% lower than the national OSHA level. ACGIH has established a threshold limit value of 25 ppm, and a short term exposure limit of 100 ppm (OSHA 2005).

Public Health

The EPA has set a maximum contaminant level (MCL) in drinking water at 0.005 mg PCE/L water (USEPA 2006). The reference dose for PCE is 0.01 mg/kg/day.

Environmental Hazards

PCE most often enters the environment via fugitive emissions from dry cleaning and metal degreasing industries and by spills or accidental releases to air, soil or water (USEPA 2006). When released to soil, PCE will evaporate fairly rapidly into the atmosphere due to its high vapor pressure and low adsorption to soil. It can leach rapidly through sandy soil and therefore may reach groundwater.

When PCE is released in water, the primary loss will be by evaporation. Chemical and biological degradation are expected to be very slow. PCE should not accumulate in aquatic organisms nor absorb onto sediment (USEPA 2006). PCE is toxic to aquatic organisms.

For releases to the atmosphere, PCE will be expected to exist in the vapor phase and will degrade through reaction with photochemically produced hydroxyl radicals or chlorine atoms produced by photooxidation of PCE (USEPA) 2006).

5.1.3 Use and Functionality

Primary applications of PCE have been as a chemical intermediate or as a solvent, as most organic materials dissolve in PCE.

Nationally, since 1998 the major use of PCE has been as the basic raw material in the manufacture of hydrofluorocarbon (HFC) 134a, a popular alternative to chlorofluorocarbon (CFC) refrigerants. It also is used in the synthesis of several hydrochlorofluoro-carbons (HCFC 123 and 124 and HFC 125). In 2004 over 66% of the 355 million pounds of PCE use was in this application.

The second most common use of PCE in 2004, dry cleaning, constituted 12% of the total PCE usage nationally. This is down from about 25% of the 344 million pounds in 1998. The decrease can be attributed to the improved efficiency of dry cleaning machines in the industry as well as the emergence of alternative cleaning processes and chemicals. PCE constitutes 70% of all commercial dry cleaning solvents.

In 2004, aerosol products (for cleaning tires, brakes, engines, carburetors and wire as well as an anti-seizing agent) made up 12% of the total use of PCE. Automotive aerosols use has remained about the same or declined slightly since 1998.

As an industrial metal cleaning and degreasing agent, the trend has been a slight decrease in the overall usage. The portion of PCE used as a vapor degreaser is now 8%. Table 5.1.3 A lists the shift in PCE usage from 1998 to 2004.

Table 5.1.3 A: Shift in National PCE Usage from 1998 to 2004
(Halogenated Solvents Industry Alliance, Inc. 2005)

PCE Use Category	% in 1998	% in 2004
Chemical intermediate	50	66
Dry Cleaning/textile processing	25	12
Automotive aerosols	10	12
Metal cleaning/degreasing	10	8
Miscellaneous	5	2

PCE Regulations

Table 5.1.3 B lists various regulations and requirements that are associated with PCE.

Table 5.1.3 B: PCE Regulations and Requirements (National Toxicology Program 2005)

Agency	Regulation and Requirements
CPSC (Consumer Product Safety Commission)	Visual novelty devices containing PCE have labeling requirements
DOT (Department of Transportation)	PCE is considered a hazardous material and a marine pollutant and special requirements have been set for marking, labeling, and transporting this material
EPA	• Clean Air Act NESHAP: Listed as a Hazardous Air Pollutant (HAP) • NSPS: Manufacture of substance is subject to certain provisions for the control of • Volatile Organic Compound (VOC) emissions • Urban Air Toxics Strategy: Identified as one of 33 HAPs that present the greatest threat to public health in urban areas • Clean Water Act • Effluent Guidelines: Listed as a Toxic Pollutant • Water Quality Criteria: Based on fish/shellfish and water consumption = 0.69 μg/L; based on fish/shellfish consumption only = 3.3 μg/L • Comprehensive Environmental Response, Compensation, and Liability Act • Reportable Quantity (RQ) = 100 lb • Emergency Planning and Community Right-To-Know Act • Toxics Release Inventory: Listed substance subject to reporting requirements • Resource Conservation and Recovery Act • Listed Hazardous Waste: Waste codes in which listing is based wholly or partly on substance - U210, F001, F002, F024, F025, K019, K020, K073, K116, K150, K151 • Characteristic Toxic Hazardous Waste: TCLP Threshold = 0.7 mg/L • Listed as a Hazardous Constituent of Waste • Safe Drinking Water Act • Maximum Contaminant Level (MCL) = 0.005 mg/L
FDA	Maximum permissible level in bottled water = 0.005 mg/L

5.2 Perchloroethylene Use Prioritization

Uses in Massachusetts Manufacturing

In Massachusetts, three of the above mentioned applications for PCE - aerosol packaging, metal degreasing and garment cleaning - were also reported in the Toxics Use Reduction Act (TURA) data for 2003. In addition, use in plating masks was reported. The maskant is used to protect areas during certain plating steps and is removed before the process is finished. This masking agent does not appear in the final manufactured product. The largest national use, manufacturing of refrigerants or HCFC's, was not reported in the TURA data, and is not a significant manufacturing use in Massachusetts.

Six companies reported use of PCE in the 2003 TURA data. This does not represent the total number of companies using PCE in Massachusetts, because small businesses (< 10 employees) and those using less than 10,000 lb of PCE are not required to report. For example, there is only one facility in the state reporting PCE used in dry cleaning (15,000 lb total use). The Massachusetts DEP works with dry cleaning facilities through their Environmental Results Program, (ERP). Under this program, DEP has identified over 550 dry cleaning facilities that use PCE. Total usage is estimated to be over 1 million pounds.

Metal cleaning and degreasing was responsible for 6% of total PCE use reported under TURA in 2003. Again, this is not representative of all PCE usage for metal cleaning and degreasing because of the high reporting threshold (10,000 lb) relative to the amount used in most facilities.

Two companies reported PCE usage in distribution, accounting for just over half of the approximately 304,000 lb of PCE used in the state. This activity typically consists of repackaging chemicals from tank wagons into smaller containers. The smaller containers are then sold to users in Massachusetts and other states for a specific end use. This study focuses on alternatives for the specific end uses, rather than for the distribution of the chemical.

The second largest reported use in the state is for custom blending of raw material, reported by one aerosol packaging facility. This use made up 34% of the PCE reported. When contacted, this facility reported that they were not packaging PCE for use in automotive aerosols at this time, but had done so in the past. While some industry experts stated that PCE was no longer used widely in many automotive aerosols, the *Household Products Database* (National Library of Medicine 2004) reports PCE being used in automotive and specialty consumer aerosol cleaners.

Total pounds of reported PCE usage in Massachusetts and the percentage from 2003 are listed in the Table 5.2 A.

Table 5.2 A: PCE TURA Reported Use 2003

(Toxic Use Reduction Institute (TURI) 2005)

PCE TURA Reported Use 2003	Total Use (lbs)	% of total
Distribution	154,207	51
Aerosol packaging	103,529	34
Metal cleaning/degreasing	19,600	6
/textile processing	15,697	5
Plating Mask	11,184	4

Uses in Products

In addition to previously mentioned applications, there are many smaller volume industrial and consumer uses of PCE. Industrial uses include paint stripping, adhesive and ink formulations, insulating fluid in electrical transformers and paper coatings. Consumer uses for PCE include furniture polish/cleaners, oven cleaners, lubricants and pesticides. Some uses frequently listed in references have been determined to be historical and are marked below as "not a current practice." Table 5.2 B lists general product types that may utilize PCE.

Table 5.2 B: Industrial and Consumer Use/Applications of PCE

Industrial Use/Application	Consumer Use/Application
Paint stripping; paint & varnish removers; consumer – not a current practice	Furniture polish/cleaners household rug & upholstery cleaners
Adhesive formulations	Non structural caulking
Printing inks	Oven cleaners
Solvent for de-inking paper	Lubricating oils & greases
Paper coatings	Laundry starch products – not a current practice
Insulating fluid in electrical transformers	Waterproofing compound Shoe polish
Silicones	Compounds & sealants
Process solvent for desulfurizing coal	Silver polish, spray
Heat-exchange fluid	Rubber coatings
Remove soot from industrial boilers	Pesticides – not a current practice

Summary of Stakeholder Input

Stakeholders raised several issues concerning the use of PCE. One of the major concerns was the exposure of workers (especially in automotive repair facilities) using aerosol PCE products for cleaning and repair work. In addition, there were concerns that many products were available to consumers and were used with limited awareness or health warnings about the potential for exposure.

In addition to automotive applications, there was strong stakeholder interest in learning more about the health implications of various dry cleaning alternative solvents that are currently available on the market. There have been several other organizations such as the Institute for Research and Technical Assistance (IRTA), California Environmental Protection Agency Air Resources Board (CARB) and the state of North Carolina that have done reports on dry cleaning alternatives in the past few years. Stakeholders were eager to have that body of information expanded upon and related to conditions in Massachusetts.

Priority Uses

Based on the analysis of national and state PCE use, stakeholder input and exposure potentials, three high priority use categories were selected. PCE is widely used in dry cleaning of garments in Massachusetts with exposure potential to workers. This combined with strong stakeholder interest led to its selection as a high priority use. Automotive aerosols were determined to be a high priority because of exposure to both workers and the general public and because of the strong interest by stakeholders.

Vapor degreasing was selected as a high priority because of its prevalence nationally and in Massachusetts and because of industry's interest in learning more about the alternatives. The Institute has a great deal of expertise in cleaning technologies and through the TURI Laboratory's work had heard from several Massachusetts companies that were searching for vapor degreasing alternative chemistries. From this work, there was an identified need to identify drop-in replacements for PCE in existing closed-loop, air-tight vapor degreasing equipment.

5.3 PCE Alternatives Prioritization

5.3.1 Alternatives Associated with Dry Cleaning

Available Alternatives for Dry Cleaning

Since the 1960s, the dry cleaning industry has predominantly used PCE as its cleaning solvent. In Massachusetts, there are over 550 dry cleaning facilities that report under DEP's Environmental Results Program. These facilities use over 73,000 gallons of PCE resulting in 600,000 pounds of hazardous waste (Peck 2005).

Currently several dry cleaning alternative chemicals and processes are available on the market, summarized in table 5.3.1. The most widely used alternatives are hydrocarbon-based systems from three manufacturers. Capitalizing on the success of these hydrocarbon systems, one manufacturer created a mixture of hydrocarbons (isoparaffins) with a hydrofluoroether and a perfluorocarbon to further enhance performance (expanded cleaning capabilities) and improve safety (by raising the flash point). Another option uses volatile methyl siloxane as the cleaning solvent. Glycol ether-based alternatives are also used to a lesser extent.

Non-solvent based alternative dry cleaning systems currently on the market include carbon dioxide and wet cleaning. Carbon dioxide, as either a liquid or a supercritical fluid, can also be used to clean garments utilizing specialized equipment. Typically, liquid carbon dioxide is maintained under a pressure of 700 pounds per square inch and uses detergents specifically designed for this process. Companies are also using wet cleaning processes for more dry-clean-only garments. These processes rely on water, detergent, conditioners and/or degreasers to clean the garment. Wet cleaning processes sometime use specialized equipment designed to minimize temperature and agitation or to create a fine mist to deliver the water-based detergents to the materials to be cleaned.

Table 5.3.1 A: Dry Cleaning Alternatives

Classification	Sample Product Names
Hydrocarbons	Exxon DF 2000 Fluid
	Chevron EcoSolv
	Shell Shellsol
	Drylene 800
Hydrofluoroether (HFE), perfluorocarbon (PFC), hydrocarbon (isoparaffins)	Pure Dry
Volatile methyl siloxane (VMS) (decamethyl cyclopentasiloxane); GE Cyclopentasiloxane	GreenEarth
Substituted aliphatic glycol ethers (dipropylene glycol tertiary-butyl ether DPTB)	Rynex
Traditional wet cleaning	Laidlaw Corporation PowerBrite detergent
Cold Spray Washing	Icy Water: DWX-44 detergent
Spray Washing	Green Jet : DWX-44 detergent
Carbon dioxide	Liquid carbon dioxide

Alternatives Screening

All eleven dry cleaning chemistries passed the initial EH&S screen for carcinogens, PBTs and TURA More Hazardous Chemicals.

Alternatives Prioritization for Dry Cleaning

In order to limit the number of alternatives studied, alternatives were prioritized using information about which alternatives were being used in Massachusetts and preliminary EH&S and technical feasibility data. Input from stakeholders was also a key factor in determining priority alternatives.

Stakeholders felt that it would be valuable to assess as many classes of commercially available alternatives as possible. Therefore, an important criterion for prioritization was to have each type or class of alternative represented in the list for final assessment.

One product, Pure Dry, was eliminated from further assessment because two of its components, hydrofluorocarbon and hydrofluoroether, had PBT concerns. Specifically, both chemicals exceed EPA's very persistent criteria for water, soil, sediment and air. In addition, HFE was in the bioaccumulative range and of moderate concern for aquatic toxicity.

Because several of the hydrocarbon alternatives were similar in their make-up, one was selected as representative of that class of alternatives. Based on the Institute's survey of Massachusetts dry cleaners, Exxon DF2000 is used more frequently than the other hydrocarbon alternatives. It is important to note that while the other two hydrocarbon alternatives (Chevron EcoSolv and Shell Shellsol) were not included in the following assessment, they would be worthy of consideration as feasible alternatives.

Drylene 800, a petroleum distillate product, was not chosen for further study because very little information could be obtained on this product. In addition, the Institute did not identify any dry cleaners in Massachusetts using Drylene 800.

Traditional wet cleaning is used by many dry cleaners in Massachusetts for some garments or when requested by customers. There are also some dry cleaners that use wet cleaning exclusively. The product options for the wet cleaning alternatives include traditional wet cleaning, Icy Water and Green Jet. Icy Water and Green Jet both use the same DWX 44 detergent.

Rynex, which is increasing used by dry cleaners in Massachusetts according to the Institute's survey, is based on substituted aliphatic glycol ethers (dipropylene glycol tertiary-butyl ether DPTB). Rynex did not approach any levels of concern in the EH&S screening.

GreenEarth was found to have some PBT levels of concern with half-lives of 340 in sediment and 31 days in air. However, due to the interest of stakeholders in GreenEarth as an alternative, and because it is the second most popular alternative for dry cleaning, behind DF 2000, based on the Institute's survey of Massachusetts dry cleaners, it was included for further assessment.

Liquid carbon dioxide is currently not as popular as many other alternatives, but was included because of its potential as a minimal-waste option with no traditional solvent used.

The screening and prioritization processes narrowed the field of possible dry cleaning alternatives to assess to the five listed on Table 5.3.1 B. These were, DF 2000, GreenEarth, Rynex, Wet cleaning with DWX 44 (including sub categories of Icy water and Green Jet processes) and liquid carbon dioxide. Products with their corresponding classifications are listed in the next table.

Table 5.3.1 B: Selected Dry Cleaning Alternatives and Classifications

Dry Cleaning Alternatives	Classification
DF 2000	Isoparaffin Hydrocarbon
Rynex	Substituted Aliphatic Propylene Glycol Ether
GreenEarth	Volatile methyl siloxane
Traditional Wet Cleaning	Aqueous based
Icy Water	Aqueous based
Green Jet	Aqueous based
Carbon Dioxide	Liquid carbon dioxide

5.3.2 Alternatives Associated with Vapor Degreasing

Available Alternatives for Vapor Degreasing

Over the years, the preferred solvent used in vapor degreasing has changed many times. Vapor degreasing solvents have included chloro-fluoro-carbons (CFCs), trichloroethane (TCA), trichloroethylene (TCE) and perchloroethylene (PCE). CFCs and TCA were found to be ozone depleting and have been phased out under the Clean Air Act. Currently, the major solvent used in vapor degreasing operations is TCE. PCE is used less often than TCE, but is still used in significant quantities.

There are many reasons why companies continue to use vapor degreasing. Many do so because of concerns about the ability of aqueous-based alternative cleaning processes to produce clean and dry parts. Further obstacles of cleaning with water based cleaning may be associated with the design and complexity of parts shapes. Due to the high surface tension of water, aqueous cleaning formulations can not always get into small, blind holes without implementing a significant process change. Solvents in the vapor form are more successful at cleaning these hard to reach areas. In some instances, the costs associated with new equipment required for alternative processes are a barrier.

n-Propyl Bromide (nPB)

Several different cleaning formulations have been developed to address the need for alternatives to PCE in vapor degreasing. The most widely used alternatives have been products based on n-propyl bromide (nPB). It should be noted that nPB was found to be a developmental toxin by the State of California and was added to their Proposition 65 list on December 2005. The chemical is also currently undergoing carcinogenicity testing by the EPA. At the same time, however, EPA has proposed allowing the use of nPB, under the Significant New Alternatives Policy program (SNAP), as a replacement for ozone depleting substances such as CFC 113, trichloroethane, HCFC 141b and more recently, TCE and PCE in vapor degreasing and other applications. Since nPB is a relatively new solvent to the global market to replace higher ozone depleting substance (ODS) solvents, new data about its toxicity is still emerging.

Halogenated Organic Alternatives

Other classes of products include those based on hydrochlorofluorocarbons (HCFCs) or hydrofluorocarbons (HFCs), which are available from a few manufacturers in varying forms. Hydrofluoroethers (HFEs) have also shown some success in vapor degreasing applications and are available in multiple formulations.

Siloxane-Based Alternatives

The last class of solvent-based alternatives identified is volatile methyl siloxanes (VMS). These products have not been as widely used for vapor degreasing but have many of the necessary physical proprieties such as surface tension and Kb[6] value.

Aqueous-Based Process Change

Switching to aqueous systems is a potentially feasible alternative to solvent-based vapor degreasing, though this option may involve additional time and capital investment. The Institute's Surface Solutions Laboratory (TURI Lab) has worked with companies to help them switch from traditional chlorinated solvents to aqueous based cleaning or alternative solvent based vapor degreasing. Each company's cleaning needs are unique and a cleaning process should be specifically tailored for those needs. Information on the success of the TURI Lab's efforts in alternative, less toxic cleaners can be found at www.cleanersolutions.org.

In a related effort to eliminate chlorinated solvent degreasing in Massachusetts, the Institute worked with the Massachusetts Office of Technical Assistance on an EPA funded grant to help companies replace chlorinated solvents in their cleaning processes. One company that received assistance during the study had switched from TCE to an nPB based cleaner but then approached the TURI Lab for help in making the next step to an aqueous cleaner. This was accomplished in 2004 and was fully integrated and implemented throughout the company and its plating lines in 2005. Details about this process are included in Appendix E.

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[6] Kauri butanol value (Kb) is a measure of the cleaning strength of a solvent. The higher the Kb, the more aggressive the solvent. For more information, see the Technical Assessment for vapor degreasing alternatives.

Table 5.3.2 A summarizes the products identified as alternatives to PCE-based vapor degreasing.

Table 5.3.2 A: Vapor Degreasing Alternatives

Classification	Sample Products
Propylbromide (nPB)	Tech Spray Solvon (IP or PB)
	Petroferm Lenium (GS, CPor ES)
	EnviroTech Ensolv
	Kyzen Metalnox 6960
Hydrochlorofluorocarbon (HCFC)	Asahi AK 225
Hydrofluorcarbon (HFC)	DuPont Vertrel MCA
	MicroCare Heavy Duty Degreaser C
	MicroCare Heavy Flux Remover C
Hydrofluoroether (HFE)	3M HFE 7100, 7200 or 71DE
Volatile methylsiloxane (VMS)	Dow OS 10, OS 20, or OS 30
Process Change	Aqueous based alternatives and systems (see case study of multi-step phase out of vapor degreasing)

Alternatives Screening

All identified vapor degreasing alternatives passed the initial EH&S screen for carcinogens, PBTs and TURA More Hazardous Chemicals. However, there were some concerns brought up during this phase of screening. The manufacturing of 2-propanol (isopropyl alcohol – an ingredient in some of the formulations) by the strong acid process is listed as a Group 1 carcinogen (carcinogenic to humans) by IARC while the chemical itself is listed as a Group 3 (not classifiable as to its carcinogenicity). The screening methodology for this project only applies to substances in the product, not to upstream or downstream processes, feedstocks or waste materials. Therefore, alternatives with 2-propanol were not screened out (because the carcinogenicity is with the manufacture of the 2-propanol only, not the chemical as it exists in the cleaning formulations), however that information was considered during the prioritization process.

Alternatives Prioritization for Vapor Degreasing

Since there were several similar products within some of the chemical classes, representative products were selected for further assessment. In addition, several products contained chemicals with high Persistence Bioaccumulation or Toxicity values or had potential carcinogenicity concerns associated with the life cycle. This information was considered during the prioritization process, noted below, when final decisions were made about which alternatives to assess.

n-Propyl Bromide (nPB)

Serious concerns regarding the toxicity of nPB were identified during the prioritization process. Even so, when stakeholders were consulted they indicated that including it in the assessment would be valuable in their efforts to compare potentially safer substitutes for PCE. Because of the pending approval of nPB under the SNAP program, products based on nPB are now frequently considered as alternatives for chlorinated solvents in many applications including vapor degreasing. Therefore, the Institute decided to include an nPB-based product in the assessment. The one nPB product that did not contain 2-propanol (EnviroTech's Ensolv) was selected for assessment.

Halogenated Organic Alternatives

The HFEs and the HCFC-based AK 225 were dropped from further review based on their high persistence. Each HFE product contained at least two components with half-lives that exceeded the EPA very persistent criteria. In addition, AK 225 contained a component that also exceeded the EPA very persistent criteria. As a result, the Institute did not consider these alternatives for further evaluation. Two of the three HFC products (the Vertrel product and one of the Microcare products) were prioritized for further assessment.

Siloxane-Based Alternatives

The Dow OS 10 VMS product was determined to be the safest alternative within the VMS category and was therefore selected for assessment. Specifically, the Dow OS20 and OS30 products exceeded the persistence criteria for sediment and air.

Aqueous-Based Process Change

TURI's Lab has had great success in helping companies change from vapor degreasing to aqueous based cleaning. Through TURI's Lab assistance and database of testing, aqueous based alternative cleaning products have been found for nearly 90% of all companies that the lab has worked with. Appendix E.1 contains a description of aqueous-based alternatives previously tested at TURI's Lab that could be used in a vapor degreasing multi-phase process change.

This approach to assisting companies in adopting alternatives is necessary because there are many possible choices for chemistries and process equipment, and the optimum alternative is dependent on the particular parts, materials and soils. Because of this, and based on the Institute's extensive experience in this field, it was determined that while aqueous cleaning remains a technically and economically feasible and safer alternative for many vapor degreasing situations, trying to choose a representative alternative for this study would not result in a meaningful comparison with the other vapor degreasing alternatives. Therefore, companies using this report to investigate alternatives are encouraged to review the materials in Appendix E.1 and contact the Institute for more specific information regarding aqueous cleaning options.

Summary of Vapor Degreasing Alternatives Prioritization

As a result of the prioritization process, the following alternative formulations were selected for further assessment and comparison to PCE: one nPB product (Ensolv), one VMS product (DOW OS 10), and two HFC products (Flux Remover C and Vetrel MCA). These products were selected as representative products of their chemical classes in order to assess a diverse set of alternatives. Products with their corresponding classifications are listed in Table 5.3.2B.

Table 5.3.2 B: Selected Vapor Degreasing Alternatives and Classifications

Vapor Degreasing Alternatives Evaluated	Classifications
Ensolv	n-propyl bromide (nPB)
DOW OS 10	Volatile methyl siloxane
Flux Remover C	Hydrofluorcarbon
DuPont Vertrel MCA	Hydrofluorcarbon

5.3.3 Alternatives Associated with Automotive Aerosols

Available Alternatives

The use of PCE in aerosols is widespread. The chemical can be found in applications ranging from adhesive applications to graffiti removal. PCE is used in aerosol cleaning products, many of which have been designed for various automotive needs. The three main uses of PCE in automotive shops include brake cleaning, engine cleaning and tire cleaning. Engine cleaning can be further broken down to products used externally and those used for more sensitive internal engine parts (*e.g.,* carburetors and fuel injection systems). This further classification in the engine cleaner category is necessary to ensure that the alternatives evaluated are appropriate for the intended engine cleaning application.

While immersion and other methods of cleaning are also available for some automotive repair applications, this study only included aerosol delivery systems and formulations. Automotive aerosols were a high priority for stakeholders because of their use and by both consumers and small businesses and strong potential for exposure. In addition, some of these products were identified through the Household Products database to contain upwards of 85 % PCE (National Library of Medicine 2004).

The list of potential alternatives identified represents a wide range of formulations. Many are based on non-halogenated solvents including toluene, heptane, acetone or petroleum distillates. Others use terpenes, glycol ethers, or aqueous surfactants. Specific information on each alternative is included in Appendix C.3 in the Alternatives EH&S Screening tables.

Table 5.3.3 A: Automotive Aerosols Alternatives

Classification	Sample Products
Brake	AMREP Inc, Misty Brake and Parts Cleaner EF
	AMREP Inc, Misty Brake Parts Cleaner II
	Bio Chem Systems BioBrake
	CRC Industries Brakleen Brake Parts Cleaner-Non-Chlorinated
	Mirachem 500 Foaming Aerosol
	ZEP Manufacturing Company Brake Wash
Engine - External	3M Citrus Base Cleaner (Aerosol)

Table 5.3.3 A: Automotive Aerosols Alternatives

Classification	Sample Products
	American Polywater Corporation Type HP™ Cleaner/ Degreaser
	AMREP Inc, Misty Coil Cleaning Foam
	AMREP Inc, Misty Safety Solvent 2000
	AMREP Inc, Misty Solvent Cleaner & Degreaser
	AMREP, Inc. Misty Heavy Duty Butyl Degreaser
	Berryman Products, Inc, New Engine Degreaser
	Bio Chem Systems Bio T Foammax
	Citrus Engine Brite Engine Cleaner & Detailer
	ECOLINK 3005 High Purity Contact & Precision Parts Cleaner
	LPS Micro X
	MicroCare Flux Remover C
	MicroCare Heavy Duty Degreaser C
	Mirachem 500 Foaming Aerosol
Engine - Internal	AMREP Inc, Misty Choke & Carburetor Cleaner II
	Malco Carburetor Cleaner Aerosol
	Malco Foamy Air Intake Cleaner Aerosol
	Malco Fuel Injector Air Intake Cleaner (Aerosol)
	ZEP Manufacturing Company Choke & Carburetor Cleaner
	ZEP Manufacturing Company ZEP Carb X (Aerosol)
Tire	AMREP Inc, Misty Detailing & Dressing Spray
	Armor All STP® Son of a Gun® One Step Tire Care
	Armor All Tire Foam (Aerosol)
	Bio Chem Systems Bio T General Purpose Foam
	Mirachem 500 Foaming Aerosol

Alternatives Screening

None of the automotive aerosols were eliminated due to the initial screening. Many, however, contain chemicals with serious environmental or health concerns; this information was taken into account during the prioritization process.

Alternatives Prioritization

For brake, engine and tire cleaners, where similar products existed within a particular chemical class, representative products were selected for further assessment. In addition, to arrive at a reasonable number of alternatives for assessment, products that contained chemicals with high values for P, B or T, or that have carcinogenicity indications, were considered a lower priority for assessment.

Brake Cleaners

Two products, ZEP Manufacturing Company Brake Wash and AMREP Inc Misty Brake Parts Cleaner II, contain 2-propanol. Due to the carcinogenicity of one manufacturing method for 2-propanol, and because there are numerous other alternatives available for assessment, these products were eliminated from further consideration.

The remaining four aerosol brake cleaner products, Bio Chem Systems BioBrake, CRC Industries Inc Brakleen Brake Parts Cleaner-Non-Chlorinated, AMREP Inc, Misty Brake and Parts Cleaner EF and Mirachem 500 Foaming Aerosol, were selected for further assessment. It should be noted that some of these products contain constituents with known hazards, for example, one product contains 43% toluene. These issues will be addressed in the EH&S assessment.

Table 5.3.3 B: Brake Cleaning Aerosol Alternatives and Classifications

Brake Cleaning Aerosol Alternatives Evaluated	Classifications
AMREP Inc, Misty Brake and Parts Cleaner EF	Heptane-Acetone mix with Carbon Dioxide propellant
Bio Chem Systems BioBrake	C9-C12 hydrocarbons; Propanol ,2-methoxymethylethoxy; Acetone;
CRC Industries Brakleen Brake Parts Cleaner-Non-Chlorinated	Toluene; Methanol; Acetone; Xylene; Heptane; n-hexane; with Carbon Dioxide propellant
Mirachem 500 Foaming Aerosol	Aqueous based with propane-isobutane propellants

Engine - External

Two products, both from MicroCare, were eliminated from further analysis as an engine cleaner because of high persistence values for the constituents tetrafluoroethane (aerosol only), pentafluorobutane and decafluoropentane. One product, Ecolink 3005 High Purity Contact & Precision Parts Cleaner was eliminated from further study because one of its constituents exceeded the EPA criteria for water, soil, sediment and air persistence.

In addition, several products were considered a lower priority for assessment based on the presence of 2-propanol or mineral seal oil (some "mineral oils, untreated and mildly treated" are an IARC Class 1 carcinogen). For the case of mineral seal oil, there was not enough information available to determine whether the mineral oils in these products are highly treated or not. For each of these alternatives, there were other products based on similar formulations, but without 2-propanol and mineral oil, that were included in the assessment. Therefore several products were eliminated: AMREP Inc, Misty Safety Solvent 2000 (2-propanol), LPS Micro X (2-propanol), and Bio Chem Systems Bio T Foamaxx (Mineral Seal Oil).

This still left seven products that represented a range of different mixtures. It was decided to include them all for final assessment. These products were Misty Heavy Duty Butyl Degreaser, Citrus Engine Brite Engine Cleaner & Detailer, 3M Citrus Base Cleaner (Aerosol), AMREP Inc, Misty Solvent Cleaner & Degreaser, AMREP Inc, Misty Coil Cleaning Foam, Mirachem 500 Foaming Aerosol and Berryman Products Inc New Engine Degreaser.

Table 5.3.3 C: External Engine Cleaning Aerosol Alternatives and Classifications

External Engine Cleaning Aerosol Alternatives Evaluated	Classifications
Misty Heavy Duty Butyl Degreaser	Aromatic Petroleum Distillates; 2-Butoxyethanol; with an Isobutane-Propane propellant blend
Citrus Engine Brite Engine Cleaner & Detailer	2-Butoxy Ethanol; Methyl Esters of C16–C18 and C18; Unsaturated Fatty Acids; Petroleum Sulfonate; Kerosene; Orange Peel Oil Sweet Cold Pressed; Nonyl Phenol Ethoxylate; Carbon Dioxide
3M Citrus Base Cleaner (Aerosol)	D-Limonene with propane propellant
Misty Solvent Cleaner & Degreaser	Monocyclic Terpene Methyl Esters Of Soybean Oil
Misty Coil Cleaning Foam	Aqueous with propane-isobutane propellants
Mirachem 500 Foaming Aerosol	Aqueous with propane-isobutane propellants
Berryman Products Inc New Engine Degreaser	Aqueous cleaner with nitrogen propellant

Engine - Internal

Again the two products from MicroCare were dropped from further analysis based on the higher persistence values for the constituents Tetrafluoroethane (aerosol only), 1,1,1,3,3-Pentafluorobutane and 1,1,1,2,3,4,4,5,5,5-decafluoropentane. Similarly, many products were considered a lower priority for assessment because of the presence of 2-propanol, mineral oil or other substances with carcinogenicity concerns. These products and constituents of concern were ZEP Manufacturing Company Choke & Carburetor Cleaner (Methylene Chloride, Ethyl Benzene), AMREP Inc, Misty Choke & Carburetor Cleaner II (2-propanol), Malco Foamy Air Intake Cleaner Aerosol (2-propanol).

Three products, ZEP Manufacturing Company ZEP Carb X (Aerosol) American Polywater Corporation Type HP™ Cleaner/ Degreaser, and Malco Fuel Injector Air Intake Cleaner (Aerosol), were selected for final assessment.

Table 5.3.3 D: Internal Engine Cleaning Aerosol Alternatives and Classifications

Internal Engine Cleaning Aerosol Alternatives Evaluated	Classifications
ZEP Manufacturing Company ZEP Carb X (Aerosol)	Toluene; Methanol; Xylene; Hydrotreated Light Petroleum Distillates
American Polywater Corporation Type HP™ Cleaner/ Degreaser	Medium Aliphatic Petroleum Solvent Monocyclic Terpene
Malco Fuel Injector Air Intake Cleaner (Aerosol)	Xylene; Toluene; Propane; Isobutane; Acetone

Tire

One tire cleaning formulation, Bio Chem Systems Bio T General Purpose Foam, contained 2-propanol and was therefore a lower priority for assessment.

The remaining four products were selected for assessment. These products are Armor All Tire Foam (Aerosol), Armor All STP® Son of a Gun® One Step Tire Care, AMREP Inc, Misty Detailing & Dressing Spray and Mirachem 500 Foaming Aerosol.

Table 5.3.3 E: Tire Cleaning Aerosol Alternatives and Classifications

Tire Cleaning Aerosol Alternatives Evaluated	Classifications
Armor All Tire Foam (Aerosol)	Silicone Emulsion; Dimethyl Ether; Propylene glycol; Propane and Isobutane
Armor All STP® Son of a Gun® One Step Tire Care	Diethylene Glycol Monoethyl Ether; Alkyloxy polyethylene oxyethanol; Isobutane; Poly dimethylsiloxane; Water
Misty Detailing & Dressing Spray	Hexane; Poly Dimethylsiloxane; Petroleum Distillates; Isobutane- Propane propellant
Mirachem 500 Foaming Aerosol	Aqueous with propane-isobutane propellants

5.3.4 Summary of Alternatives Prioritization

Almost all of the alternative chemical formulations for the high priority uses selected for PCE passed the initial screening criteria of the TUR More Hazardous List, EPA or IARC carcinogen, and PBT limit values. Products were then selected for full assessment based on preferable screening results, professional recommendations and representation from different classes of formulations.

5.4 PCE Alternatives Assessment

5.4.1 Alternatives Assessment for Dry Cleaning

Technical Assessment

Dry cleaning practices must meet certain industry expectations for various operating parameters. These conditions include operating times, amount of clothes cleaned, quality of cleaning, compatibility with a wide range of clothing materials, pre-spotting requirements, and post cleaning handling (pressing, etc.).

The overall cleaning ability of a process depends on soil chemistry, textile fabric type, transport medium (aqueous vs. non-aqueous), chemistry of the additives (detergents, surfactants), the use of spotting agents, and process considerations (California Air Resources Board 2005).

Additional solvent properties to consider include evaporation rate and ease of purification through distillation. The solvent should not cause fabric to unnecessarily fade, shrink, weaken, or bleed color and should be compatible with detergents (California Air Resources Board 2005).

Each alternative is summarized briefly below. For more detailed descriptions of the different technologies, see Wolf and Morris, 2005.

Summary of Alternatives

The alternative processes and chemistries to be assessed are listed in Table 5.4.1A.

Table 5.4.1 A: Dry Cleaning Alternatives

Alternatives	Classification	General Name
DF 2000	Isoparaffin Hydrocarbon	HC
GreenEarth	Volatlile methyl siloxane	VMS
Rynex	Substituted aliphatic glycol ethers	SGE
Wet Cleaning - traditional	Aqueous based	Wet Cleaning
Wet Cleaning -Icy Water	Aqueous based	Icy Water
Wet Cleaning -Green Jet	Aqueous based	Green Jet
Carbon Dioxide	Liquid carbon dioxide	CO_2

Hydrocarbon (HC – DF 2000)

Hydrocarbon technology is the most widely used alternative to PCE Dry cleaning. The industry has a long history of using petroleum solvents as the industry relied on them for cleaning garments and other items prior to switching to the nonflammable PCE. The new version of the HC cleaning materials are most often isoparaffins, synthetic hydrotreated aliphatic hydrocarbons. DF-2000 is a combustible liquid (flashpoint >38° C and <93° C) with a flashpoint of 64° C.

The equipment for use with the new HC solvents is different from the equipment used with PCE because of HC's low flash point. Some of the machines are equipped with a refrigerated condenser (for vapor recovery) while others are not. Distillation of the HC is done in a vacuum to adjust for the higher boiling points. Initial cycle times of HC machines were longer than they were for PCE; however manufacturers have been working on reducing the process times to match those for PCE.

One issue with the HC solvent is that the use can support bacteria growth. Systems using the HC should remain free of water. The control of water can be accomplished by using an absorbent material such as Tonsil®. This additive may also eliminate the need to distill and may reduce the need to add detergents during cleaning (Wolf, Morris 2005).

Volatile Methyl Siloxanes (VMS - GreenEarth)

GreenEarth is a volatile cyclic methyl siloxane (VMS) and is a combustible liquid with a flash point of 76.7°C. As was the case for HC, VMS based solvents need to be used with equipment that is designed to handle combustible solvents. Newer equipment has been designed with larger and increased extraction speeds that work to reduce the cycle time. Due to VMS physical characteristics, the separation of the solvent and water can be difficult and separators for use with the technology have been designed to address this challenge (Wolf, Morris 2005).

Substituted Aliphatic Glycol Ethers (SGE - Rynex)

The substituted glycol ethers have a flash point of >93° C and is not considered a combustible solvent. However, equipment must be designed to handle solvents with a flash point. Cleaning does not require additional detergents as the glycol ethers are capable of removing oil-based and water-soluble soils.

Distillation is difficult for this solvent due to the interaction with water. The solvent is miscible in water and has a similar specific gravity making separation more challenging. The traditional combustible solvent equipment must be modified to route the water to one chamber and the glycol ether to another based on their boiling point differences. The separation process is slow. However, manufacturers have claimed that the equipment problem has been solved (Wolf, Morris 2005).

Aqueous Based Wet Cleaning (Traditional – PowerBrite)

Professional wet cleaning has been available to dry cleaners for more than a decade. It relies on water, conditioners, degreasers and detergent for cleaning the garments. Despite the wide use of this type of cleaning, only a few cleaners have adopted the technology as an exclusive cleaning method.

Equipment generally consists of a computer controlled washer and dryer and specialized finishing units called tensioning equipment. To prevent dimensional change and to make finishing easier, many garments are not completely dried leaving a residual of moisture. The tensioning equipment is then used to help to form garments and restore constructed garments to their final or original shape during finishing and helps to prevent them from shrinking. Disadvantages of wet cleaning are that cleaners must learn entirely new processing methods (Wolf, Morris 2005).

Aqueous Based Wet Cleaning (Icy Water- DWX 44)

This technology is similar to traditional wet cleaning but has been designed to control shrinkage and minimize tensioning. Like traditional wet cleaning, the icy water technology relies on water, detergent, conditioners and degreasers to accomplish cleaning. The process operates at a temperature of 38° F and is dried with cold air. In addition, the garments are agitated at one revolution per minute in the washer and only 60 revolutions per minute in the dryer, much slower than in the traditional aqueous process.

Aqueous Based Wet Cleaning (Green Jet – DWX 44)

This aqueous process involves the use of chemical cleaning and drying in one machine. Cleaning takes place using a mist of water and detergent. The garments are not immersed in liquid. The machine cycle is shorter than the cycle for PCE but can only be used for garments that are lightly soiled. The detergent used for this process, as well as Icy Water is predominantly DWX 44 (Wolf, Morris 2005).

Carbon Dioxide (CO_2)

This process relies on liquid carbon dioxide under a pressure of 700 lb/in^2 to clean garments. Because of the pressure used the equipment is expensive and costly to maintain; it is made of stainless steel and must be capable of withstanding significant pressure. During cleaning, the system is pressurized prior to the cleaning cycle and depressurized after the cleaning cycle. The equipment may include filters for removing particulate contaminants and a distillation unit for separating the soluble contaminants. The detergent used in the carbon dioxide process is relatively expensive and is described by some cleaners who use the technology as not aggressive enough.

The carbon dioxide used in the process can be stored in a bulk tank onsite or a service can be used which regularly changes out the empty tanks when more carbon dioxide is needed. The most common equipment requires a large amount of space yet there are some machines that are about the same size as a traditional PCE machine (Wolf, Morris 2005).

While CO_2 is known to be a green house gas, the CO_2 used for dry cleaning is captured as a byproduct of industrial production. There is no overall net increase in CO_2 emitted to the atmosphere and therefore does not contribute to global warming overall (California Air Resources Board 2004).

Emerging Technologies

Household dry cleaning, air-cleaning and textile alternatives are emerging technologies. While sufficient information to conduct an alternatives assessment was not available, a brief description is provided at the end of this section.

Performance Criteria

Performance information was drawn largely from two sources. One source was the *Evaluation of New and Emerging Technologies for Textile Cleaning* conducted by the Institute for Research and Technical Assistance (IRTA) that was prepared for the California Air Resources Board and the U.S. Environmental Protection Agency in 2005(Wolf, Morris 2005). In order to relate the California study to Massachusetts Dry cleaning companies and to collect additional information, site visits and interviews were used to gather information from local businesses using either PCE or an alternative. The Korean Dry Cleaners Association expressed interest in providing information to support the assessment, and a project assistant fluent in Korean made many site visits to their member's facilities. The Northeast Fabricare Association also expressed a willingness to share information and several site visits were made to their members as well.

Two types of site visits were conducted. Initial site visits set out to determine the profile of the industry in regard to the use of PCE and the alternatives. Over thirty facilities completed questionnaires regarding current dry cleaning practices. A summary table of these visits is listed in Table 5.4.1 B. In addition a copy of the questionnaire filled out by the dry cleaners can be found in Appendix E.1 along with a short summary of the drycleaner's comments.

Table 5.4.1 B: Dry Cleaning Preliminary Data Collection

Location	Years in Operation	# of Employees	Machine Generation	Solvent Use	Past PCE Use	Gallons/ year	Spotting Chemical
Leominster	3	Full: 2 Part:1	4th	PCE		30	No PCE
Leominster	9	Full: 2 Part:0	5th	PCE		40	No PCE
Westborough	2	Full: 2 Part:2	3rd	PCE		70	No PCE
Methuen	18	Full: 3 Part:2	4th	PCE		60	No PCE
Canton	1.5	Full: 5 Part:1	4th	PCE		150	No PCE

Table 5.4.1 B: Dry Cleaning Preliminary Data Collection

Location	Years in Operation	# of Employees	Machine Generation	Solvent Use	Past PCE Use	Gallons/ year	Spotting Chemical
Salem	13	Full: 2 Part:3	3rd	PCE		100-140	No PCE
Newton	10	Full: 2 Part:1	4th	PCE		100	No PCE
North Attleborough	5	Full: 2 Part:0		Hydrocarbon (DF2000)	Never	450-500	No PCE
Beverly	10	Full: 3 Part:3	4th	PCE		60	No PCE
Dracut	15	Full: 2 Part:2	2nd	PCE		65-70	No PCE
Stoneham	2	Full: 2 Part:2	4th	PCE		40	No PCE
Stoneham	18	Full: 6 Part:1	5th	PCE		140	No PCE
Arlington	15	Full: 1 Part:3	3rd	PCE		100	No PCE
Townsend	9	Full: 2 Part:1		PCE		30	No PCE
Newburyport	9	Full: 4 Part:0	3rd	PCE		70	No PCE
Waltham	1	Full: 1 Part:2		Hydrocarbon (DF2000)	7 years ago	150	No PCE
Haverhill	18	Full: 2 Part:1		Rynex	Before Jan, '05	35	No PCE
Northborough	7	Full: 3 Part:3	4th	PCE		25	No PCE
West Concord	6	Full: 3 Part:0	5th	PCE		60	No PCE
Concord	2	Full: Part:		Siloxane (Green Earth D5)	2 years ago		No PCE
Westborough	12	Full: 2 Part:2		Hydrocarbon	4 years ago	20-25	No PCE
Shrewsbury	3	Full: 4 Part:2	3rd	PCE		70-80	No PCE
Ruxbury	10	Full: 2 Part:1	4th	PCE		10	No PCE
West Boylston	2	Full: 4 Part:2		Hydrocarbon (DF2000)	2 years ago	20	No PCE
Leominster	1	Full: 2 Part:	4th	PCE		40	No PCE

Table 5.4.1 B: Dry Cleaning Preliminary Data Collection

Location	Years in Operation	# of Employees	Machine Generation	Solvent Use	Past PCE Use	Gallons/ year	Spotting Chemical
		3					
Wilmington	9	Full: 3 Part: 0	4th	PCE		65	No PCE
Acton	8	Full: Part:		PCE		75	No PCE
Chelmsford	6	Full: Part:	4th	PCE			No PCE
Woburn	7	Full: Part:		Siloxane (Green Earth D5)	7 years ago	60	No PCE
Stoughton	16	Full:1 Part: 3		PCE		80	No PCE

The second type of site visit was designed to gather information from companies that had made the switch to one of the alternatives being reviewed in the assessment. During these visits, information on past and present cleaning practices and benefits and drawbacks to the alternatives was collected. Six alternative evaluation site visits were conducted. Location and dry cleaning solvents used are listed in Table 5.4.1C.

Table 5.4.1 C: Dry Cleaning Alternative Evaluation Site Visits

Solvent Used	Location
PERC	Nashua, NH
Hydrocarbon	Quincy, MA
Hydrocarbon2	Waltham, MA
Green Earth	Charleston, MA
Rynex	Haverhill, MA
Wet Cleaning	Arlington, MA

Operating Time

The operating time for dry cleaning includes time to run the machine for cleaning and drying (designated as cleaning time). It does not include loading, unloading, pre- and post spotting. In order to compare each process to a PCE system, the average cleaning time for each system was divided by the time for PCE cleaning. Any process that took longer than PCE would have a normalized time greater than one. Of the alternative processes reviewed only two had shorter cleaning times. These were Green Jet and CO_2 cleaning, both of which require little to no drying times. The most popular alternative, HC cleaning, requires about one third more time for the cleaning process.

The IRTA study measured operating times for each of the alternatives. The Institute supplemented the IRTA data with information from Massachusetts facilities. The Massachusetts site visits documented times for cleaning that were slightly longer than those found in the IRTA Study. The only Massachusetts based process that had an improved operating time was the drycleaner using the HC process. They switched from a “hard mount” system, taking over an hour to clean, to a “soft mount" method reducing their cleaning time to under an hour. The soft mount allowed for a faster drum rotation during the drying portion. The VMS process was used at two visited locations. One of those no longer uses the process as they were unsatisfied with performance and times. Their cleaning time was over 2.5 times longer than with their PCE system. A qualitative comparison of the various methods from both the IRTA study and the Massachusetts site visits are in Table 5.4.1D.

Table 5.4.1 D: Operating Time Qualitative Comparison

Process	Time (min) California Facilities	Normalized Rate		Time (min) Massachusetts Facilities	Normalized Rate	
PCE	45	1		45	1	
HC	60	1.33	-	55	1.22	-
VMS	62	1.38	-	73	1.62	-
				120	2.67	-
SGE	63	1.40	-	66	1.47	-
Wet Cleaning	65	1.44	-	60	1.33	-
Icy Water	long drying					
Green Jet	30	0.67	+			
Carbon Dioxide	30	0.67	+			

Comparison Key + Better = Similar - Worse ? Unknown

Load Capacity

Most of the manufacturers of the dry cleaning equipment, including the alternative processes, offer equipment with various load capacities. Based on supplied literature, the data from the IRTA Study, and Massachusetts site visits, the available load capacity ranges were used in this study to determine an average load in pounds. Some members of the Korean Dry Cleaning Association noted that they run their machines based on the quantity of clothing cleaned and were less concerned about operating times. They went on to say that they use most of their machines at approximately 80% capacity to ensure proper cleaning and that no damage will be done to the machines due to overloading. Therefore these calculations were made in an attempt to determine the number of loads that could be run as compared to typical or past PCE systems.

The average value for PCE was used to normalize the alternatives to the PCE load capacity. In this situation, processes with values greater than one would have a larger cleaning capability and likewise, those with a normalized capacity less than one would have a lower load capacity. The IRTA Study revealed that on average, three alternative dry cleaning systems would have an equal or greater capacity, with all of the processes comparable to PCE systems, ranging from 0.86 to 1.12.

From the Massachusetts site visits a separate load capacity average was found for PCE based on the actual capacities used at the locations. The HC facility reported an average load capacity that was

33% greater than their previous PCE system, and 50% greater than the average PCE system for all facilities. The VMS system being used at the Massachusetts site had a capacity of 50 lb but the system was only operating at 40 lb at a time to ensure proper cleaning. The normalized capacity at 40 lb was three-quarters of the average PCE system. This load capacity was similar to that being used in the SGE system. A qualitative comparison of the load capacities of the various processes from both the IRTA Study and the Massachusetts site visits are in the following Table 5.4.1E.

Table 5.4.1 E: Load Capacity Qualitative Comparison

Process	California Facilities	Average Load			Massachusetts Facilities	Average Load		
	pounds	pounds	Normalized Load		pounds	pounds	Normalized Load	
PCE	35-65	50	1		45-60	53	1	
HC	35-50	43	0.86	-	80	80	1.51	+
VMS	46-66	56	1.12	+	40	40	0.75	-
SGE	35-50	43	0.86	-	40	40	0.75	-
Wet Cleaning	30-70	50	1	=	12		0.27	-
Icy Water	55	55	1.1	+				
Green Jet	45	45	0.9	-				
Carbon Dioxide	45	45	0.9	-				

Comparison Key + Better = Similar - Worse ? Unknown

Cleaning Quality

The cleaning quality comparison revealed that many of the alternative processes were not as aggressive as PCE. In general, this results in a reduced efficiency in cleaning. The HC system operators visited in Massachusetts indicated that they had problems with water soluble soils and water contamination from spotting chemicals and detergents. The VMS facility operators stated that they had to sacrifice some of their cleaning capabilities when using the alternative to PCE. Comparison of the various methods from both the IRTA Study and the Massachusetts site visits are given in Table 5.4.1F for soil removal.

Table 5.4.1 F: Soil Removal Comparison		
Process	**Soil Types California Facilities**	**Massachusetts Facilities**
PCE	Relatively aggressive cleaner for oil based soils	
HC	Not as aggressive as PCE for grease and oil contaminants	Issues with water soluble soils
VMS	Less aggressive for oil based contaminants than PCE	Lost some cleaning performance
SGE	Aggressive solvents for oil based contaminants; They can remove water soluble soils very effectively	
Wet Cleaning	Aggressive cleaning method; effective on both oil based and water soluble soils	
Icy Water	Same advantages as the traditional wet cleaning technology	
Green Jet	Effective for lightly soiled fabrics	
Carbon Dioxide	Many oil based contaminants are soluble - similar to HC	

Garment Compatibility

The information gathered from the IRTA Study was for the most part consistent with what was found during the Massachusetts site visits. PCE is capable of cleaning a wide range of materials, although it sometimes has trouble with leather, suede, beaded materials and many delicate garments. The Massachusetts HC facility operators stated that they had trouble with maintaining silk sheen whereas the IRTA Study implied that the HC process would be able to clean silks well. This Massachusetts company also found they needed to do more lint removal prior to cleaning. However, this effort was offset with having to do less lint removal after cleaning.

The VMS facility operator stated that they were able to clean just about any fabric; what they could not do with the VMS they also could not previously do with PCE. The user of the SGE process found that they were now able to do beaded materials when their PCE system could not. Both processes (PCE and SGE) had trouble with leather and suede. Comparison of the various methods from both the IRTA Study and the Massachusetts site visits are presented in Table 5.4.1G for clothing compatibility.

Table 5.4.1 G: Clothing Compatibility

Process	Clothing types California Facilities	Massachusetts Facilities
PCE	Compatible with numerous textiles	Trouble with leather, beads, suede
HC	Delicate garments like silks, wedding gowns, drapes, suede and leathers and beaded garments	Had trouble with silk sheen. More lint control up front but less afterward
VMS	Delicate items can be cleaned	Can do just about any fabric including suede & leather trim. What it can not do, (rain coats) neither could PCE
SGE	Wide range of fabrics; safe for most beads, sequins, buttons, trimmings, vinyl	Can do beads that PCE could not. Can not do leather and suede
Wet Cleaning	Delicate items like wedding gowns and suede and leather garments	Limitation of garment materials that could be cleaned; trouble cleaning leather, suede, rayon and some types of wool
Icy Water	More forgiving than traditional wet cleaning; Wools, Silks, Spandex, Leather, Suede, Real/Fake Fur, Gowns with decorative beads and trim -	
Green Jet	Clean garments that are currently sent out or that can't be cleaned with other solvents	
Carbon Dioxide	Gentle cleaner; Some materials, like vinyl, rubber or beads, swell during the cleaning process; Some acetate materials cannot be cleaned; fur and leather can be cleaned	

Spotting and Post Handling

In most forms of dry cleaning spotting agents are usually used to remove the spots before dry cleaning takes place in the machine. PCE is an aggressive solvent, it is easy to use and it is very forgiving. Even when a cleaner is not especially good at spotting, the PCE machine will remove many stains. After the cycle is completed, the garments, which are fully dry, are removed from the machine and finished with standard equipment (Wolf, Morris 2005).

The IRTA study reported that PCE and TCE were found in the effluents of some of the wet cleaning facilities used in the study. The origin of the contamination, sometimes in concentrations high enough to classify the waste as hazardous, was surmised to be either cross contamination with the PCE dry cleaning machines or the spotting agents being used on the clothing. From the data gathered from over two dozen site visits in Massachusetts, the facilities reported that no TCE or PCE based spotting agents were used. In the past this was not the case, according to Peter Blake of Northeast Fabricare Association. He stated that there had been efforts made to guide dry cleaners away from spot cleaners containing PCE and TCE. The dry cleaning industry responded by creating alternatives to replace spotting agents containing these chlorinated solvents. These spotting chemicals are typically tailored for a specific soil type eliminating the need for a universal spotting agent (traditionally PCE based).

The IRTA Study data for spotting and post handling were adjusted for this study so that the times were all based on a uniform amount of clothes cleaned per hour. As with the cleaning times and load capacities, these qualitative rates were normalized based on a PCE system. For these performance criteria, systems requiring less time would have a normalized value less than one and systems requiring more time would have a normalized value greater than one.

According to the data from the IRTA Study, three of the processes required about twice as much pre-spotting time. The SGE system claimed to need only a fraction of the time that PCE required for cleaning. For post cleaning only VMS and carbon dioxide required more effort than PCE. When comparing the overall pre and post handling times, SGE, wet cleaning and carbon dioxide all resulted in time savings.

The qualitative comparison of the various methods for spotting and post handling from both California and Massachusetts site visits is given in Table 5.4.1 H. The numbers in the table are times relative to that for PCE.

Table 5.4.1 H: Pre-Spotting and Post Handling Qualitative Comparison

Process	Pre Spotting California Facilities		Post Cleaning Finishing California Facilities		Combined pre/post California Facilities		Massachusetts Facilities	
PCE	1		1		1			
HC	1.81	-	0.63		1.22	-	>1	-
VMS	2.39	-	1.24	-	1.81	-	>1	-
SGE	0.08	+	0.01	+	0.04	+	1.20	-
Wet Cleaning	0.72	+	0.88	+	0.80	+		
Icy Water								
Green Jet	2.03	-	0.86	+	1.44	-		
Carbon Dioxide	0.56	+	1.17	-	0.87	+		

Comparison Key + Better = Similar - Worse ? Unknown

The Massachusetts site visits yielded more qualitative information about the individual processes. The HC facility found that they needed more effort on spotting for grease-based soils. They had to retrain their workers to address the spotting issues that arose with this system. Furthermore, the facility had to add a second spotting station. They continued to use the same spotting agents that they were using for PCE.

The workers interviewed at the VMS facility found spotting to be more difficult, since they had to utilize specially formulated spotting agents that were compatible with the VMS solvent and supplied to them by the solvent manufacturer. They found that these new spotting agents were not as effective as those used with PCE cleaning.

In the SGE plant the spotting process was taking two minutes longer than the PCE system, an increase of 20% in labor time. This increase is significant as labor costs can be upwards of thirty percent of the overall cost of dry cleaning and is by far the most expensive component of the total process.

Many of the issues for spot cleaning were similar to what was found for the various processes in the collected technical information from the IRTA report, the various manufactures' literature and Massachusetts site visits as shown in Table 5.4.1 I.

Table 5.4.1 I: Massachusetts Site Visit Pre-Spotting and Post Handling Qualitative Comparison

Process	Technical Information Review	Massachusetts Facilities
PCE		
HC	"Hand" or the feel of the garments cleaned with HC is better than the hand of garments cleaned with PCE.	More spotting effort, grease spots - retrain workers, same spotting agents
VMS	More spotting is likely to be required, very good hand better than HC	Spotting difficult; Spotters less aggressive, not as good, more effort, different spotting agents
SGE	Finishing of the garments which may contain high concentrations of water could be more difficult	20% more spotting time, use less spotting agents, less post spotting
Wet Cleaning	Prevent dimensional change; wet garments are hung and later finished using tensioning equipment	50% more time for spotting
Icy Water	Minimize or eliminate garment shrinkage; tensioning equipment but does not need to use it for finishing the garment	
Green Jet	Spotting is more difficult, finishing is much easier than for other technologies	
Carbon Dioxide	More spotting is required; post spotting instead; similar to finishing requirements with PCE	

Recycling

The recycling process for the HC facility was found to require less maintenance than the previously used PCE process. The distillation unit was easier to clean as it had less oily residue baked onto the unit. The PCE process required workers to chip away at the hardened material whereas the HC process required no chipping or hard labor to remove the solid waste. The bulk could be picked up and the residual removed with a rag.

The VMS operator stated that the distillation process was inefficient and time consuming. They have plans to lease new machines that come without a distillation system. Instead of distilling, the company plans to institute a new process using filter material called Tonsil®.

Tonsil® filter powder is produced from bentonite then enhanced by an acid process producing very fine clay with highly adsorbent properties. Typically, Tonsil® is used in combination with diatomaceous earth. Both compounds are placed on a typical nylon spin disk filter. The additive can adsorb dyes, water soluble soils, solvent soluble soil, moisture and fatty acids from the solvent. Tonsil® also exhibits an inhibiting property for reducing or eliminating corrosion and bacteriological growth (Childers 2004). This process would require the filters to be cleaned each day and reportedly could eliminate the need to distill the cleaning solvent.

The SGE facility does no distillation of their cleaning solvent and disposes of the solvent as a hazardous waste. Comparison of the various methods from both the IRTA Study and the Massachusetts site visits are presented in Table 5.4.1J.

Table 5.4.1 J: Dry Cleaning Solvent Recycling Comparison

Process	From Literature Review	Massachusetts Facilities
PCE	PCE, which is heavier than water, is physically separated from the water.	Re-deposition issues (likely related to particular distillation process)
HC	Distillation of the HC must be performed in a vacuum. Tonsil® filters may make distillation unnecessary	Distillation maintenance was easier than PCE as it created less build up on the distillation unit
VMS	Separation of the solvent and water is more difficult	Distillation changed the cleaning chemical; Expect to eliminate the need to distill by using Tonsil® filtering process.
SGE	Problems for the water separation process	Not distilling
Wet Cleaning		Not applicable
Icy Water		Not applicable
Green Jet		Not applicable
Carbon Dioxide		Not applicable

Wastewater

Wet Cleaning operators in Massachusetts must adhere to the state's Title V regulations that prohibit commercial discharge to septic systems. A commercial wet cleaner, drycleaner, or laundry may not discharge gray water to a septic system. In addition, these industries can only discharge to the ground with a groundwater discharge permit.

Financial Assessment

Data were collected during the site visits on costs associated with dry cleaning. When looking at machine costs, the alternative solvent process machines were found to be 40 to 50% more expensive than PCE machines. The wet cleaning facility reported a lower purchase price for their equipment when compared to PCE.

Likewise the alternative solvent cost was also greater than PCE, ranging from 25% greater to twice the cost; the wet cleaning process used more detergents and water, but no solvents. One HC facility was paying more for their detergent but another HC facility was paying about the same. The SGE facility was using no additional detergents and only had the solvent to purchase. From the VMS process, costs for solvent and detergents were about the same as what they were spending when they used PCE.

Despite the fact that nearly all of the alternative facilities were paying about the same price for spotting agents (SGE was 67% less), spotting labor costs were all greater than when using a PCE based system. Spotting expenses with VMS were found to be sixty percent more.

Maintenance requirements were higher in both the HC plants resulting in an increase in operating costs. This increase would likely also apply to a CO_2 facility due to the specialized maintenance required for equipment. The wet cleaning facility reported a 60% decrease in maintenance needs and expenses. The SGE location had yet to spend any money or time on maintenance on its relatively new machine (14 months). VMS maintenance resulted in an increase in costs.

Utility expenditures were roughly equal to the PCE based dry cleaning process. For some alternatives there were minor to moderate increases of 25-35%. Some of the facilities stated that their utility costs were the same.

Most of the companies spent the same or less time on regulations and paperwork. The SGE process resulted in a 60% decrease in the amount of hazardous wastes generated. Wet cleaning created no hazardous waste. The other processes generated about the same amount of hazardous waste as the PCE process. All companies that had to dispose of hazardous waste were paying the same rate per drum with the same waste handler as they had been for PCE removal.

The costs comparisons for the various Massachusetts locations surveyed are included in Table 5.4.1 K. Additional information on the economic comparisons can be found in Appendix E.1.

Table 5.4.1 K: Costs Comparisons for Massachusetts Facilities

Location	**U[7] Cleaners**	**C Cleaners**	**D Cleaners**	**L Cleaner**	**T Cleaners**
Process	Wet Cleaning	HC	HC	SGE	VMS
Machine cost	Less	More	40% more	50% more	45% more
Solvent Cost	None	35% less	27% less	100% more	Same
Cost of detergent	100% more	100% more	Same	None	Same
Spotting agent cost	Same	Same	Same	67% less	Same
Spotting labor cost	50% more	30% more	60% more	20% more	60% more
Maintenance of equipment	60% less	40% more	60% more	None	Same
Overall cost of maintenance	60% less	40% more	60% more	None	Same
Water	Same	25% more	Same	None	Same
Gas	30% more	25% more	Same	Same	Same
Electricity	35% more	25% more	Same	Same	Same
Paperwork required per week		None		50% less	Less
Regulation-Compliance Costs	Same	None	None	Same	
Licenses			None		$3,250

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[7] Facility names will be included pending approval from facilities.

Table 5.4.1 K: Costs Comparisons for Massachusetts Facilities

Location	U[7] Cleaners	C Cleaners	D Cleaners	L Cleaner	T Cleaners
Hazardous Waste Disposal	None	Same	Same	67% less	Same
Hazardous Waste Costs	Same	Same	Same	Same	Same

None - potential for savings, Same - equal costs, Less - cost savings, More - greater costs

Despite the increases in operating costs for many of the alternative processes, the price the consumer was charged for cleaning the garment remained the same.

Environmental Assessment

Several key factors, including persistence, bioaccumulation and toxicity potential, were reviewed to determine the environmental profile of dry cleaning solvents. Further information on environmental parameters and levels of concern are included in Appendix A; detailed data for dry cleaning alternative chemistries are included in Appendix D.3.

The persistence and bioaccumulation potentials were estimated using the EPA PBT profiler. The aqueous based detergent did not have a specific list of constituents that could be assessed. The persistence of the solvents in water was low, less than 60 days. Persistence in soil for the alternatives was found to be high except for carbon dioxide. VMS, SGE and PCE were all in the persistent range. The HC solvents were found to be at the borderline of being very persistent, with a value of 180 days. For sediment persistence, the alternatives had shorter residence times than PCE, although the VMS and SGE were still very persistent. There was no value determined for the HC solvent due to the limitations of the tool. None of the alternatives had persistence in air exceeding PCE's 93 days except carbon dioxide.

The modeled bioaccumulation factors for most of the alternatives and PCE were below the EPA listed criteria for bioaccumulative. A log K_{ow} value was estimated for the HC solvent (6.6-7.0 using the EPI program (SRC, EPA, EPI (Estimation Programs Interface) Suite http://www.epa.gov/opptintr/exposure/docs/episuite.htm) for hexane (C6H12). The estimated log K_{ow} was 6.6 to 7.0, which indicates a higher affinity for lipids (fat cells) than for water, and potential for bioaccumulation.

According to the MSDS for PCE, the solvent is considered to be toxic to fish. None of the alternatives exceeded the threshold for aquatic toxicity.

If the solvents are incinerated at their end of life, combustion by-products may be produced. Combustion byproducts of PCE may include hydrogen chloride and phosgene. Many of the alternatives break down into carbon dioxide, carbon monoxide and oxygen.

PCE is a NESHAP, whereas none of the alternatives are. None of the assessed products, including PCE, were listed by the EPA as ozone depleting chemicals. Carbon dioxide was the only greenhouse gas, but as previously stated CO_2 is generally not created especially for use as a dry cleaning solvent and therefore does not add to net greenhouse gas emissions.

Human Health Assessment

Acute Effects

PCE has a PEL of 100 ppm. The only other alternative that had a listed PEL was carbon dioxide with a value of 5000 ppm. Two of the other alternatives have an REL listed. The HC's REL was 171 ppm and VMS was 10 ppm. There is no PEL or REL for SGE.

According to the NIOSH Pocket Guide to Chemical Hazards PCE can irritate the skin, the eyes and the respiratory track. Similarly, according to MSDS for the water based product and SGE, these two alternatives can cause the same types of irritation. From the MSDS for VMS and carbon dioxide, neither will result in irritation to the skin, the eyes and the respiratory track. In sufficient concentrations, carbon dioxide is an asphyxiant. The HC solvent MSDS states that the solvent may produce eye irritation including watering and redness as well as mild skin irritation. Respiratory irritation is not expected to occur

Chronic Effects

Long term hazards examined include mutagenicity, carcinogenicity and reproductive and developmental toxicity. The EPA has classified PCE as reasonably anticipated to be a human carcinogen and IARC lists the solvent as category 2A, probably carcinogenic to humans. PCE is also listed for cancer on California's Prop 645. In contrast, the alternatives are not classified by EPA or IARC with regard to carcinogenicity.

In June of 2005 the Silicones Environmental, Health and Safety Council of North America (SEHC), the European Silicone Industry (CES) and the Silicones Industry Association of Japan (SIAJ) released a White Paper on Health Research Findings of Decamethylcyclopentasiloxane (D5), the Dry cleaning solvent used in the VMS system. Two consistent reported adverse effects of D5 exposure in rats have been increased liver weights in male and female rats and also an increase of uterine endometrial adenocarcinoma tumors in female rats at the highest concentration (160 ppm for 24 months), while no adverse effects were observed in male rats (Silicones Environmental, Health and Safety Council of North America (SEHC); European Silicone Industry (CES); Silicones Industry Association of Japan (SIAJ) 2005). The authors hypothesize that the liver weight increase is due to an increase in liver enzyme production in order to process and eliminate D5 from the rat's body and is reversible, and do not expect to see the same effect in humans. To date there has been no known peer review or outside scientific analysis of the findings.

PCE can damage the eyes, skin, respiratory system, liver, kidneys and the central nervous system. SGE affects the eyes, skin and central nervous system. High concentrations of carbon dioxide can affect the respiratory system, cardiovascular system, lungs, skin and central nervous system.

Other Hazards

Flammability and Flash Point

PCE is considered to be non-flammable and has no flash point. Based on the National Fire Protection Association (NFPA) rating system PCE has a zero fire hazard, whereas both the HC solvent and VMS have a rating of 2. The HC has a flash point of 64° C and VMS's flash point is 76.7° C. SGE has a NFRP fire rating of one with a flash point greater than 93° C. Like PCE, carbon dioxide and the various water based detergents have a fire rating of zero and no flash points.

In the context of worker health and safety, PCE and the water based cleaners pose no auto-ignition and fire hazard in the work place while the HC, VMS and SGE solvents all possess flashpoints under 93° C and are considered combustible and carry with them a possibility of fire near an ignition source of a spark or open flame. A fire hazard may also be a factor if the machinery possesses a leak and solvent vapors accumulate to a dangerous level and could ignite.

Reactivity

All of the dry cleaning solvents had a NFPA reactivity rating of zero which would signify that the products are stable when exposed to heat pressure or water.

Corrosivity

Corrosiveness was measured using pH values. Products with a pH less than 2 and greater than 12 would be considered to be corrosive. Products with no pH, (PCE, HC and VMS), would not applicable to this measurement of corrosivity. SGE had a pH of 7. The Aqueous based product had a pH of 8.5 at a 1% concentration. All solvents fall within a range that is safe for workers in the case of an accidental spill

Summary of Dry Cleaning Alternatives

As demand increases for alternatives to PCE in dry cleaning, manufacturers of the alternative cleaning equipment and chemistries have been working to address many of the issues that still exist, such as longer cleaning cycles, limited soil removal and garment compatibility.

Table 5.4.1 M summarizes the technical, economic, environmental persistence, human health and other hazards that are associated with the alternative processes and compares them to the current practice of using PCE for dry cleaning.

In the table a "+" sign denotes a benefit associated with the alternative process. A "-" symbol implies that the alternative had a characteristic that was not as desirable as PCE. When the alternative process was comparable to the traditional solvent an "=" was used. In some cases when multiple facilities provided information on a process, observations were made that were not the same at both facilities. In these instances, two symbols could appear in the comparison table. For any criteria that was not found or unknown, a "?" was used.

Based on the gathered data from the alternative site visits, most of the alternative processes took longer for the cleaning process, and may not be as universally applicable to different soils and garment materials as PCE. In addition, VMS, substituted glycol ether and carbon dioxide had slightly higher costs than a PCE system, whereas HC and wet cleaning were equivalent to PCE.

The data in Table 5.4.1 M shows that overall, the alternative solvents were less persistent in the environment than PCE. From a human health perspective, most of the alternatives are preferable or equivalent to PCE. It should also be noted that there is a lack of toxicological data on some of the alternatives.

The major concern that existed for many of the alternatives was flammability. Only water cleaning and carbon dioxide were equal to PCE with no fire hazard. The other alternatives all possessed flashpoints and were rated as combustible, thus requiring specialized equipment to protect against fire or explosion.

Table 5.4.1 L: Assessment Summary for Dry Cleaning Alternatives

Assessment Criteria		PCE reference	HC	VMS	SGE	Wet Cleaning	Carbon Dioxide
Technical Criteria	Time	45 min	-	-	-	-	+
	Load capacity	60 lbs	-	+	-	+/-	=
	# of Soils		-	-	=	-/=	=
	Clothing types		+	=	+	-	-
	Spotting requirements		-	-	=/-	-	+
Financial Criteria	Equipment		-	-	-	+	-
	Solvent		+	?	-	+	?
	Labor		-	?	=	-	?
	Operating		=	?	=	=	?
	Regulatory		+	=	+	+	+
Environmental Criteria	Water	60 days	+	+	+	+	+
	Soil	120 days	-	+	+	+	+
	Sediment	540 days	+	+	+	+	+
	Air	98 days	+	+	+	+	-
	BCF	83	-	+	+	+	+
Human Health Criteria	Exposure limits	100 ppm; 25 TLV	+	-	?	+	+
	Dermal/Oral/Respiratory	Irritant	?	+	=	=	+
	Mutagenicity	No	=	=	=	=	=
	Carcinogenicity	2A	+	+	+	+	+
	Repro/Develop Tox	No/?	=	=	=	=	=

Table 5.4.1 L: Assessment Summary for Dry Cleaning Alternatives

Assessment Criteria		PCE reference	HC	VMS	SGE	Wet Cleaning	Carbon Dioxide
Safety Criteria	Flammability	Nonflammable	-	-	-	=	=
	Reactivity	Non reactive	=	=	=	=	=
	Corrosivity	Non corrosive	=	=	=	=	=

Comparison Key + Better = Similar - Worse ? Unknown

Emerging Dry Cleaning Alternatives

Household Dry Cleaning

These in-home products provide a convenient system that delivers fresh clothes in about 30 minutes. The products are reported to remove stains and odors and help minimize wrinkles. Most garments are purportedly ready to wear with little or no ironing. These do-it-yourself kits include a pre-spotting stain remover with blotting pads to absorb the stain. Odors are removed by a gentle steaming caused by the moist dryer sheet and the heat of the dryer. Manufacturers claim that they can be used on items such as sweaters, blouses, blazers, dresses, slacks and vests. They can be used on fabrics that include wool, rayon, silk, linen, acetate and blends of these fabrics. One of these alternatives, Dryel, states that it is safe for brass buttons, shoulder pads or sequins but should not be used on leather, suede, velvet, or fur, or with large items that do not have room to tumble freely.

More information on two existing home dry cleaning products can be found at Procter and Gamble Dryel - (http://www.dryel.com/using/index.html) and Clorox™ FreshCare™ Dry Clean and Gentle Fabric Cleaning - (http://www.cloroxfreshcare.com/dryclean.html).

The home dry cleaning kit does not offer a viable substitution for professional pressing. In addition, neither kit is as effective as traditional dry cleaning for removing more serious stains. The International Fabricare Institute (IFI), the leading association representing the cleaning industry, disputes some of Dryel's claims. Earlier this year, IFI published a report on Dryel, concluding that while the product does remove odors and is effective on water-soluble stains, it is not as effective as dry cleaning in stain removal (International Fabricare Institute (IFI)).

When subjected to the same parameters in the summary table, these products do not provide the same level of cleaning as dry cleaning but do cost less and take less time for certain applications. Sufficient information was not available from the products' Material Safety Data Sheets (MSDS) to provide an environmental, health and safety profile.

Air-cleaning

"Aircleaning" could join dry cleaning and wetcleaning as a possible option for garment cleaning. A "concept appliance" was designed by students in Singapore. This waterless washing process, called Airwash, won the Design Lab Award in a competition sponsored by Electrolux to develop appliances for the future based on satisfying consumers' needs and trends.

The Airwash prototype unit developed by the students uses negative ions, compressed air and deodorants to clean clothes. The device would eliminate detergents and water from the cleaning process. More information on the air cleaning process can be found at the National Clothesline Magazine, December 2005 issue.

Textile Alternatives

The need for dry cleaning originates with the textile and garment manufacturers. Using textiles that can be wet cleaned, or are compatible with alternative cleaning solvents, will reduce the need for solvent-based dry cleaning. Other emerging technologies for textiles include chemical treatments that reduce the ability of a stain or odor to penetrate the fabric, or that eliminate the need for pressing. It should be note, however, that these fabric treatments may contain formaldehyde, fluoropolymers, nanomaterials or other substances that warrant further investigation.

5.4.2 Alternatives Assessment for Vapor Degreasing

Many of the companies still using vapor degreasing are doing so because they believe that the aqueous-based alternative cleaning processes will not work for them, either for performance or equipment compatibility. There are also companies that may be willing to switch to an alternative less toxic cleaning process, including an aqueous system, but due to other barriers, such as managerial concerns, cost and resource constraints, process changes have not been pursued.

Solvents in the vapor form have shown to be successful in reaching hard-to-clean areas; these unique situations may still require the use of vapor degreasing cleaning processes. Site visits conducted by the Institute and the Office of Technical Assistance (OTA) over the last few years found very few companies using open top vapor degreasing equipment. Most facilities had invested resources into the use of closed-loop airless degreasers.

PCE is generally used in degreasing operations because of its high boiling point or chemical stability. Its high boiling point allows the solvent to remove soils and waxes that lower-boiling solvents may not. The stability of the chemical makes it particularly useful in airless degreasing systems where low emissions mean less virgin solvent and stabilizers being added.

Under an EPA grant awarded to the Institute and OTA, the TURI Laboratory compared the vapor degreasing alternatives listed in Table 5.4.2 A below, as well as many others, to the physical properties and cleaning performance of PCE and other chlorinated solvents.

Under the grant, site visits were conducted to determine what type of cleaning equipment was being used for vapor degreasing. For the companies that were using older open-top degreasing systems, the researchers were able to identify chemical alternatives that were as effective at cleaning as vapor degreasing and could be used with the existing equipment after minor modifications. One company changed from a vapor degreasing cleaning operation to cleaning with ultrasonic energy and a new chemistry by retrofitting the existing equipment

Other facilities were using more advanced, closed-loop systems recently purchased at high capital cost to the company. While these companies were open to the idea of substituting for PCE and other chlorinated solvents for cleaning, the sizable investment in existing equipment mandated its use. This required TURI's Lab to investigate other solvents with the required physical characteristics necessary for vapor degreasing solvents.

Table 5.4.2 A: Vapor Degreasing Alternatives

Vapor Degreasing Alternatives Evaluated	Chemical Type	Components	Code
Ensolv	n-propyl bromide (nPB)	n-Propyl bromide; Stabilizer package	nPB
DOW OS 10	Volatlile methyl siloxane	Hexa-methyldisiloxane	VMS
Flux Remover C	Hydrofluorcarbon	1,1,1,3,3-pentafluorobutane; 2,3-dihydrodecafluoropentane; trans-1,2-dichloroethylene Methanol	HFC1
DuPont Vertrel MCA	Hydrofluorcarbon	2,3-dihydrodecafluoropentane; trans-1,2-dichloroethylene	HFC2

Background on NPB, N-Propyl Bromide

N-propylbromide, or bromopropane is a non-flammable organic solvent with a strong odor. It is used to remove solder flux, wax, oil, and grease from electronics parts, metals, and other materials. In addition, nPB is used as a solvent in adhesive formulation. NPB has a low ozone depletion potential (ODP) of 0.013, and EPA is proposing to allow the use of nPB as a chemical alternative to other higher level ozone-depleting substances (ODS) under the SNAP program with certain conditions (USEPA) 2003).

NPB, has been reported to be a severe neurotoxin and NTP is currently conducting a two year inhalation study to test nPB for carcinogenicity potential. The chemical was added to California's Prop 65 list and the California Department of Health Services Hazard Evaluation System and Information Service (HESIS) issued a health alert for nPB in 2003 and 2004. HESIS issued the Hazard Alert because nPB "is being considered for widespread use and has not been regulated to protect workers, consumers, or the environment" (HESIS) 2003).

Background on VMS, Volatile Methyl Siloxanes

VMSs are mild combustible solvents, and possess a moderate level of toxicity with a manufacturer's recommended exposure level of 200 ppm. Because the cost is high, it is generally used for defluxing and/or degreasing high value parts and electronic components. It may be used for cold cleaning and wiping or in vapor degreasing equipment. Open top vapor degreasers are not suitable and would require retrofitting (Arthur D. Little Global Managment Consulting 1999). It should be noted that the VMS solvent used in vapor degreasing is not the same chemical that is used in Dry cleaning.

Background on HFC, Hydrofluorocarbon

Hydrofluorocarbons (HFCs) are compounds containing carbon, hydrogen, and fluorine. HFCs are often blended with trans-1,2-dichloroethylene (trans-DCE) to improve solvency. Because the HFCs contain no chlorine or bromine they do not directly affect stratospheric ozone. Although it is believed HFCs will not deplete ozone within the stratosphere, this class of compounds has other adverse environmental effects. Concern in particular over global warming impacts (according to the EPA, 2,3-dihydrodecafluoropentane has a GWP of 1610) may make it necessary to regulate production and use of these compounds at some point in the future. Such restrictions have been proposed in the Kyoto Protocol (Montzka 2004).

Technical Assessment for all Alternatives

Key physical properties for a vapor degreasing solvent include: low vapor pressure, low latent heat, low boiling point, low flash point, low surface tension and high solvency powers (typically Kb values are used as a representative of this characteristic – see discussion below). In addition, product alternative performance must be equal to or greater than the current vapor degreasing solvent. Physical properties for PCE and its alternatives are shown in Table 5.4.2.B, and discussed briefly below. Values were obtained from the material safety data sheets from the appropriate manufacturers.

Table 5.4.2 B: Physical Properties of PCE and Alternative Vapor Degreaser Solvents

Product	Vapor Pressure (mm Hg)	Latent Heat (cal/g)	Boiling Point (°C)	Flash Point (°C)	Surface tension (dyne/cm)	Kb value
PCE	15.8	50.1	121	none	32.3	90
nPB	139	58.8	70	none	25.9	129
VMS	42.2	293	100	-3	15.2	16.6
HFC 1	488	~45	36	none	18.1	75
HFC 2	464	43.3	39	none	15.2	35

Low vapor pressure will help to reduce potential air pollution due to solvent evaporation. All of the alternatives reviewed had higher vapor pressure than PCE.

Latent heat corresponds to the amount of energy required to cause a substance to change from one state to another (liquid to gas). The lower the value, the less energy needed to create a vapor for cleaning. Two products, HFC1 and HFC2, have lower latent heat values than PCE. Another product, nPB, had a slightly higher value than PCE. Only one product was significantly higher than PCE; the VMS product has a latent heat nearly six times that of PCE.

In addition to the latent heat, energy savings can be obtained by using a solvent with a low boiling point. PCE's boiling point was the highest of the evaluated solvents, boiling at 121° C. In contrast, the two HFC solvents boil at a temperature just less than 40° C.

PCE and three of the four alternatives did not have a flash point. The only product evaluated with a flash point was VMS, and its flash point was very low, -3° C. Concerns over flammability significantly limit the applicability of this particular VMS solvent.

For cleaning hard to reach areas, as is the case in most vapor degreasing applications, solvents should have low surface tension in order to clean any small spaces or unusual geometries of a part. The solvent would also be able to evaporate out of these tight spaces leaving no soil or residue behind. All of the alternatives had lower surface tensions than PCE and make them favorable for cleaning complex geometric parts.

Identifying effective alternatives can be a very challenging task. A quick check to see if an alternative might be acceptable is to use its Kb value. The Kauri-Butanol (Kb) value, an ASTM method, is used to compare the strength of organic solvents (used in paint and lacquer formulations). The higher the Kb value, the more effective the solvent should be. However, there is no guarantee that a high Kb value will result in success and a low Kb does not always indicate that the solvent will be ineffective. The nPB product has a higher Kb value than PCE. The other three alternatives have lower Kb values than PCE.

The values for the six physical properties discussed are summarized in Table 5.4.2 B, which includes PCE and the four alternative products. Values were obtained from the material safety data sheets from the appropriate manufacturers.

As mentioned previously, there is no easy way short of actual testing to determine if an alternative vapor degreasing product will work for a specific cleaning situation. By reviewing the above mentioned physical properties, however, the chances of finding a product that will work will be improved.

As part of the work conducted during the EPA funded study for replacing chlorinated solvents in cleaning applications the cleaning performances of several alternatives was measured for specific situations in Massachusetts companies. The tests utilized actual soils, consisting of various oils (soils 1-5, 8-11), a rust preventative coating (soil 6) and a paint/varnish mix (soil 7). In all situations, the soils were being removed from metal parts.

All of the alternatives worked very well on the four soils that were previously being cleaned in a PCE-based system. The solvents removed over 90% of the soils for all but one soil with one cleaner. The HFC1 removed 87% of soil 1.

In the other cleaning performance evaluations, the alternatives were again very effective for the various oils. Only one soil was not effectively cleaned by all of the alternatives. Soil 7, the paint/varnish mix was only removed by one alternative, nPB. The other products were less than 15% effective in removing this mix. Table 5.4.2 C contains the summary of the testing conducted on each alternative.

Table 5.4.2 C: Laboratory Performance of PCE and Alternative Solvents against 11 Soils

Product	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Soil 7	Soil 8	Soil 9	Soil 10	Soil 11
PCE	E	E	E	E	NT	NT	NT	NT	NT	NT	NT
nPB	99.98	99.88	99.43	99.98	100.0	100.2	98.60	100.0	100.1	100.0	99.70
VMS	99.95	99.33	100.06	91.43	98.90	99.10	10.60	97.40	99.90	99.60	99.70
HFC 1	87.04	99.50	100.01	98.97	99.90	100.8	-4.90	100.4	100.7	100.3	100.6
HFC 2	93.99	98.53	99.32	99.27	100.1	100.0	-5.10	100.1	99.80	100.2	100.0

E – Effective; NT – Not tested

Note: Results of table are in percents based on gravimetric analysis.

Note: Values greater than 100 are due to minor fluctuations in the balance.

Note: Values that are less than zero signify swelling of the contaminant due to the absorption of the solvent.

Financial Assessment

Purchase prices for all of the alternatives investigated for vapor degreasing applications were found to be greater than the purchase price of PCE. The cost of PCE is approximately four dollars per gallon. The n-propyl bromide products can cost up to three times as much as PCE. The other three alternatives are considerably more expensive, at 30 to 40 times as much as the PCE baseline. Many of the listed prices in Table 5.4.2 D are approximate costs. Depending on the volume of product be purchased the prices may go down; the prices may also go down in the future if overall demand and production increase.

Table 5.4.2 D: Cost Comparison of Alternatives

Product	$/gallon	Normalized
PCE	4.31	1
nPB	13	3
VMS	123	29
HFC1	150	35
HFC2	184	43

Although the current purchase costs are substantially higher, the alternative chemicals can be more competitive with PCE when other operating costs and environmental, health and safety benefits are considered. As mentioned in the PCE replacement study in Appendix E.1, operating a vapor degreaser with nPB created a savings in energy requirements as the alternative system operated at a lower temperature. In addition to energy savings, this company was also able to extend the life of the cleaning solvent by 66%, thus reducing the amount of virgin solvent they would need to purchase to operate their system. Little information exists on operating cost comparisons for VMS and HFCs as they are not yet widely used in closed loop vapor degreasing operations.

Environmental Assessment

Several key factors were reviewed to determine the potential environmental impact of vapor degreasing solvents. Further information on environmental parameters and levels of concern are included in Appendix A; detailed data for vapor degreasing alternative chemistries are included in Appendix D.3. Initially, all products including PCE were analyzed using the EPA PBT profiler to determine persistence and bioaccumulation potentials.

Both nPB and VMS had low persistence in water, with a half-life of 15 days. The other two alternatives, HFC1 and HFC2 were very persistent (180 days), both greater than PCE at 60 days. Again nPB and VMS had low persistence in soil, both with 30 day half-lives. HFC 1 and HFC 2 had long half-lives in soil, 360 days. PCE is very persistent in sediment, having a half-life of 540 days and would make the soil or ground water hazardous if PCE is spilled. NPB and VMS are considered persistent, with sediment half-lives of 140 days. Once more, the HFC 1 and HFC2 half-lives for sediment persistence were higher than PCE. All of the products investigated were considered to be persistent in air with nPB and VMS having the shorter half-lives, 14 and 12 days respectively.

Bioaccumulation factors for the alternatives and PCE were all below the EPA threshold for a substance to be considered bioaccumulative.

According to the MSDS for PCE, the solvent is considered to be toxic to fish. VMS had the lowest value (0.062 mg/L) and would therefore be of high concern for toxicity under EPA's PBT Profiler (<0.1). Both HFC1 and HFC2 had a value of 0.6 mg/L, which would be moderately toxic. Similarly nPB was moderately toxic with a ChV of 8.5 mg/L but was closer to the low toxicity range (>10 mg/l).

The various vapor degreasing solvents reviewed were not found on the EPA list of ozone depleting chemicals. Each of the alternatives and PCE are SNAP approved except nPB which is currently being considered for approval. However some of the products do have global warming potential. Three of the alternatives have low global warming potential (no specific value given but listed as "low"), while HFC2 had a global warming potential of 806 (CO_2 = 1).

Human Health Assessment

There is less acute and chronic health information available for the alternative solvents than for PCE. The following sections summarize the limited information that is available for these alternatives.

Acute Effects

PCE has an established PEL of 100 ppm. Two components of product HFC1, methanol and trans-1,2-dichloroethylene, have PELs of 200 ppm. Some products had an REL or TLV recommended by the manufacturers on the MSDS. NPB had a TLV of 10 ppm, lower than PCE's TLV of 25 ppm. VMS had a manufacturer exposure limit from Dow of 200 ppm. A third component of HFC1 had an REL of 200 ppm as did the second component of HFC2. In summary, Table 5.4.2 E presents PEL, REL and TLV values for PCE and each alternative, for either the component with the lower value or for the complete product.

Table 5.4.2 E: Exposure Limits

Product	PEL (ppm)	REL (ppm)	TLV (ppm)
PCE	100		25
nPB			10
VMS		200	
HFC1		200	
HFC2		200	200

All of the alternatives and PCE had similar effects on the skin, eyes and respiratory tract.

Chronic Effects

N-propyl bromide can cause eye and skin irritation and redness. Ingestion of a large amount can cause abdominal pain, nausea and vomiting. Elevated inhalation of nPB can cause respiratory tract irritation, CNS depression and anesthetic effects. Prolonged exposure may cause lung, liver and kidney damage. Extended skin exposure may lead to pain, cracking and dermatitis. There is no definitive information available regarding cancer or reproductive effects in humans but many studies have found evidence of carcinogenicity and reproductive effects in test animals. California added nPB to its Proposition 65 list in 2004 as a developmental toxin. NTP is currently conducting a two year inhalation study to test nPB for carcinogenicity potential.

In 2003, the Hazard Evaluation System & Information Service (HESIS) of the California Department of Health Services issued a health hazard alert for nPB (HESIS 2003). A recent study reported that five workers who glue foam cushions together with an nPB-based glue developed severe neurological symptoms, some of which may be permanent (Majersik 2004).

Volatile Methyl Siloxanes can cause adverse health effects when inhaled or ingested. These chemicals can also cause eye and skin irritation and redness. High levels of exposure can cause dizziness, disorientation and shortness of breath. Overexposure to skin can cause de-fatting and drying of skin leading to dermatitis. Repeated ingestion can cause internal injuries. There is insufficient information available on VMS cancer effects.

Hydrofluorocarbons can cause eye and skin irritation, pain, redness and swelling. HFC's may also cause blurred vision, shortness of breath, confusion, dizziness and weakness. High acute exposure can cause unconsciousness, cardiac irregularities and death. Prolonged inhalation exposure can cause liver and lung damage, may cause heart muscle damage, chemical pneumonia and pulmonary edema. This class of chemicals has not been listed as a carcinogen by IARC, NTP, NIOSH, OSHA or ACGIH.

Other Hazards

Flammability and Flash Point

PCE is considered to be non flammable and has no flash point. Based on the NFPA rating system PCE has a zero fire hazard. According to NIOSH, n-propyl bromide has an NFPA rating of three for fire, however, the manufacturer of nPB states that the product is not flammable and has no flash point. The VMS solvent being assessed has a very low flash point, less then -3° C and an NFPA rating of three for fire hazard. It would not be appropriate for open-top vapor degreasers. Both HFC1 and HFC2 have no flash points and have an NFPA fire hazard rating of zero.

Therefore, this VMS solvent would be used in only very specific cases for vapor degreasing, where other alternatives were not effective.

Reactivity

PCE, nPB and VMS all have an NFPA Reactivity rating of zero. The other two products would be considered unstable when heated and therefore have a reactivity rating of one based on the NFPA system.

Corrosivity

Corrosivity was measured using pH values. Products with a pH less than 2 and greater than 12 would be considered corrosive. Products with no pH, such as PCE, would not applicable to this measurement of corrosivity. NPB and HFC1 both have a neutral pH. The pH values for VMS and HFC2 have not been determined.

Summary of Vapor Degreasing Alternatives

Vapor Degreasing Alternatives

The alternative vapor degreasing alternatives were found to have comparable technical features to PCE. Cleaning effectiveness was similar to PCE for removing various manufacturing soils.

Two alternatives, nPB and VMS, had lower persistence in the environment. However, the two HFCs had longer residence times. Only nPB had a lower bioaccumulation factor than PCE. The two HFC's also have potential to cause global warming.

Little human health data were found for the alternatives. Each alternative has the same irritant potential as PCE for the skin, eyes and respiratory tract. One product, VMS, had a higher PEL than PCE. The two HFCs did not have an established PEL but did have a better profile when looking at the mutagenicity, carcinogenicity and reproductive-developmental toxicity. In contrast, the nPB and VMS products had no such data that could be compared to PCE. As previously stated nPB was added to the Prop 65 list in California December of 2005 as a reproductive toxicant. NPB is currently being investigated as a carcinogen and for reproductive toxicity and mutagenicity by the NTP. A proposal by EPA is pending to list nPB under the EPA SNAP program.

These products currently cost more to purchase than PCE, creating an initial barrier for companies looking to switch to an alternative vapor degreaser. Operating conditions may help to offset this higher purchase price. Many of the alternatives would require lower operating temperatures than PCE to achieve the same level of cleaning performance.

Table 5.4.2 F contains the data for major areas of performance, costs, environmental persistence and human exposure. Both HFC 1 and HFC 2 are more persistent than PCE, but are not carcinogens. Because VMS and nPB are relatively new alternatives with no significant body of toxicological research they are listed as unknowns for most of the human health categories. Further toxicological research is necessary in order to determine whether they are safer alternatives.

Table 5.4.2 F: Assessment Summary for Vapor Degreasing Drop-In Alternatives

Assessment Criteria		**PCE reference**	**NPB**	**VMS**[1]	**HFC1**	**HFC2**
Technical Criteria	Vapor Pressure	15.8 mm Hg	-	-	-	-
	Latent Heat	50.1 cal/g	-	-	+	+
	Boiling Point	121 °C	+	+	+	+
	Flash Point	None	=	-	=	=
	Surface tension	32.3 dyne/cm	+	+	+	+
	KB value	90	+	+	-	-
	Performance	Effective	=	=	=	=
Financial Criteria	Purchase	$4.31/gallon	-	-	-	-
	Energy[2]		+	=	+	+
Environmental Criteria	Water	60 days	+	+	-	-
	Soil	120 days	+	+	-	-
	Sediment	540 days	+	+	-	-

Assessment Criteria		**PCE reference**	**NPB**	**VMS [1]**	**HFC1**	**HFC2**
	Air	98 days	+	+	-	-
	BCF	83	+	-	-	-
Human Health Criteria	Exposure limits	100 ppm PEL; 25 ppm TLV	-	+	?	?
	Dermal/Oral/Respiratory	Irritant	=	=	=	=
	Mutagenicity	No	?	?	=	=
	Carcinogenicity	2A	?	?	+	+
	Rep/Develop	No	?	?	=	=
Safety Criteria	Flammability	Nonflammable	-/=	-	=	=
	Reactivity	Non reactive	=	=	-	-
	Corrosivity	Non corrosive	=	=	=	?

Comparison Key + Better = Similar - Worse ? Unknown

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1 Not for open top vapor degreasing
2 Energy Savings based on latent heat requirements and boiling point.

Non-Vapor Degreasing Alternatives

The safest alternatives are likely to be: seeking an alternative cleaning process such as aqueous or semi-aqueous, working within the supply chain to change the contaminant on the part that is requiring the cleaning or investigate a materials change to prevent contamination and cleaning altogether. These options would likely be preferable to using PCE or any of the solvent drop-in alternatives. The case studies in Appendix E are examples of successful transitions to aqueous cleaning systems.

5.4.3 Alternatives Assessment for Automotive Aerosols

Automotive shops have utilized PCE aerosols in several end uses. One area has been in cleaning applications. The main categories reviewed in this study for PCE aerosol cleaning are tire cleaning, brake cleaning and engine cleaning. The last group was broken down further to look at products used for general external cleaning and for more sensitive cleaning of internal engine parts (carburetors, etc.). As mentioned in the alternatives prioritization section, the assessment was limited to formulations using aerosol delivery systems.

According to one manufacturer of aerosol cleaning products, the major use in the automotive industry for PCE-based aerosols is for brake cleaning. Their perspective is that tire and engine cleaning are no longer a significant use of PCE-based aerosols. While cleaners for each use were identified in the Household Products Database that included PCE as an ingredient, research and expert input have indicated that currently available brake and parts/engine cleaners are much more likely to contain PCE than tire cleaners.

Technical Assessment

Brake Cleaning

The characteristics of an effective aerosol brake cleaner involve several areas: performance, drying, and residue. Aerosol brake cleaners are used with a "spray and go" approach. As part of the cleaning process, road dirt, grease and oils must be cleaned off. Also, fibers from brake pads need to be wetted and removed safely. The end user is trying to complete the job as fast as possible. The aerosol cleaners need to clean well and evaporate quickly while leaving no residue behind. Approximately one-half to one full can is required per job (two sets of brakes).

The following four aerosol brake cleaners, listed in Table 5.4.3 A, were assessed as alternatives to PCE-based products. Products in the table will be referred to by the first or main component and the investigated use (see "Text Identification" column in table).

Table 5.4.3 A: List of Alternative Brake Cleaners

Brake Cleaning	**Sample Product**	**Constituents**	**Text Identification**
	AMREP Inc, Misty Brake and Parts Cleaner EF	Heptane-Acetone mix with Carbon Dioxide propellant	Heptane-Brake
	Bio Chem Systems BioBrake	C9-C12 hydrocarbons; Propanol ,2-methoxymethylethoxy; Acetone;	Hydrocarbon-Brake
	CRC Industries Brakleen Brake Parts Cleaner-Non-Chlorinated	Toluene; Methanol; Acetone; Xylene; Heptane; n-hexane; with Carbon Dioxide propellant	Toluene-Brake
	Mirachem 500 Foaming Aerosol	Aqueous based with propane-isobutane propellants	Aqueous 1

Information was gathered from product technical datasheets and labels to determine performance characteristics. The data collected were not based on technical performance testing as this was not available in the literature and was not within the scope of this study. Information was gathered from MSDS's, technical data sheets, industry experts and previously published reports on automotive aerosols. TURI does however recognize that testing in the lab as well as in the field is a further research need in this area in order to identify effective, less toxic alternatives.

The technical performance criteria included soil removal (oil, grease, and dirt), the control of fibers, drying times, and the lack of any residue. Each desired criteria was considered to be met if the literature for the product explicitly listed it as an attribute of the product. If it was not listed, performance was inferred from other information on the sheet. For example, the fiber control was not met by Heptane-Brake because the literature described the delivery as a powerful blasting spray. This could result in the fibers becoming airborne, increasing the inhalation exposure potential. For Aqueous 1 drying time and residue it was assumed that the foam would be designed to remain on the surface for an extended period of time.

All of the products claimed to meet the most crucial criteria of removing oil, grease and dirt. However, only one product specifically mentioned the ability to control fibers from becoming airborne during the cleaning process. It is possible that many of the alternatives could wet the fibers enough to be able control the release into the surrounding air. Collected information on each product is presented in the Table 5.4.3 B.

Table 5.4.3 B: Brake Cleaning Performance Comparison

Product	Oil, grease, dirt	Fiber control	Drying time	Residue
Heptane-Brake	Y	N - Powerful blasting spray		
Hydrocarbon-Brake	Y		Y	Y
Toluene-Brake	Y			Y
Aqueous 1	Y		N	N - Creates foam- need rinsing

Y = Yes, according to manufacturer's claims

N = No, unlikely to meet performance criteria

Blank = no information available from literature

Engine Cleaner

The use of PCE in engine cleaning applications has traditionally not been a high volume application. This limited use was due to the differing requirements for cleaning engine parts. In contrast to the brake cleaning, engine cleaners can remain on surfaces, and so don't have to evaporate quickly. The ability to cling to a surface was another desirable attribute of this cleaning process that differed from brake cleaning.

According to an industry expert, even though water-based products have been shown to work in many instances for general external engine cleaning, water based products are still not well accepted because they frequently need additional mechanical agitation (*i.e.,* scrubbing) to achieve adequate cleaning performance. In addition the water-based aerosol products tend to require rinsing after cleaning is complete.

For internal engine cleaning applications, the chemicals used must be registered as a fuel additive. Traditionally, these products have been based on methylene chloride. Some of the other products that are commonly used for engine cleaning include kerosene and Stoddard solvents. For both internal and external uses, products need to have a high flash point.

Products selected for comparison are listed in the Table 5.4.3 C. Products in the table will be referred to by the first or main component and the investigated use.

Table 5.4.3 C: List of Alternative Engine Cleaners

Engine Cleaning External	**Sample Product**	**Constituents**	**Text Identification**
	Misty Heavy Duty Butyl Degreaser	Aromatic Petroleum Distillates; 2-Butoxyethanol; with an Isobutane-Propane propellant blend	Petroleum 1-Engine
	Citrus Engine Brite Engine Cleaner & Detailer	2- Butoxyethanol; Methyl Esters of C16–C18 and C18; Unsaturated Fatty Acids; Petroleum Sulfonate; Kerosene; Orange Peel Oil Sweet Cold Pressed; Nonyl Phenol Ethoxylate; Carbon Dioxide	Butoxyethanol-Engine
	3M Citrus Base Cleaner (Aerosol)	D-Limonene with propane propellant	Terpene 1-Engine
	Misty Solvent Cleaner & Degreaser	Monocyclic Terpene Methyl Esters Of Soybean Oil	Terpene 1-Engine
	Misty Coil Cleaning Foam	Aqueous with propane-isobutane propellants	Aqueous 2
	Mirachem 500 Foaming Aerosol	Aqueous with propane-isobutane propellants	Aqueous 1
	Berryman Products Inc New Engine Degreaser	Nitrogen Propellant	Aqueous 3
Engine Cleaning Internal	ZEP Manufacturing Company ZEP Carb X (Aerosol)	Toluene; Methanol; Xylene; Hydrotreated Light Petroleum Distillates	Toluene-Engine
	American Polywater Corporation Type HP™ Cleaner/ Degreaser	Medium Aliphatic Petroleum Solvent Monocyclic Terpene	Petroleum 2-Engine
	Malco Fuel Injector Air Intake Cleaner (Aerosol)	Xylene; Toluene; Propane; Isobutane; Acetone	Xylene-Engine

Each product selected was found to meet the needs for the specific soils that were associated with engine cleaning. Only three of the products stated that they were designed to cling to vertical surfaces. One of the products was designed to leave behind a residue that would create a protective layer. This film was intended to make subsequent cleaning easier as it would prevent build up from occurring. Another product, even though it was a foam-based cleaner, was made to be free rinsing using only condensate from the air to remove the foam from the surface. The comparison of selected products for the designated performance criteria is listed in Table 5.4.3 D.

Table 5.4.3 D: External Engine Performance Comparison

Product	Oil, grease, dirt	Cling to Surface	Residue
Petroleum 1-Engine	Y	Y - Light foam	
Butoxyethanol-Engine	Y		Y - Leaves protective layer
Terpene 1-Engine	Y		
Terpene 1-Engine	Y		
Aqueous 2	Y	Y - Foam	Y - Self rinsing
Aqueous 1	Y	Y - Foam	N -Must rinse
Aqueous 3	Y		

Y = Yes, meets criteria according to manufacturer's claims

N = No, not expected to meet criteria

Blank = no information available from literature

PCE has been a minor use for carburetor, fuel injector and air intake cleaning with methylene chloride as the cleaning solvent of choice. Technical requirements include the ability to remove the appropriate soils and there are requirements that the cleaner be registered as a fuel additive. The performance criteria for internal aerosol engine cleaning products are listed in Table 5.4.3 E.

Table 5.4.3 E: Internal Engine Performance Comparison

Product	Oil, grease, dirt	Fuel Additive Registered
Toluene-Engine	Y	Y
Petroleum 2-Engine	Y	
Xylene-Engine	Y	

Y = Yes, meets criteria according to manufacturer's claims

N = No, not expected to meet criteria

Blank = no information available from literature

Tire Cleaner

Tire cleaners are used for aesthetic cleaning of rims to remove dirt and brake dust build up. PCE was found as an ingredient in some consumer based tire cleaning products in the Household Products Database, although the use of such formulations does not appear to be wide spread in businesses. One industry representative stated that PCE-based aerosol products were not used for tire cleaning by most of the businesses he supplied to. More often, the major component of tire cleaning has been ammonium bifluoride which aids in the removal of brake dust from the tire rims.

Ideally, industry experts state, tire cleaning formulations should not be corrosive; avoiding high or low pH values. In addition, cleaners should leave tires with a shine and require minimal effort for cleaning.

Products to be assessed are listed in the Table 5.4.3 F. Products in the table will be referred to by the first or main component and the investigated use except for the aqueous based product.

Table 5.4.3 F: List of Alternative Tire Cleaners

Tire Cleaning	Sample Product	Constituents	Text Identification
	Armor All Tire Foam (Aerosol)	Silicone Emulsion; Dimethyl Ether; Propylene glycol; Propane and Isobutane	Silicone-Tire
	Armor All STP® Son of a Gun® One Step Tire Care	Diethylene Glycol Monoethyl Ether; Alkyloxy polyethylene oxyethanol; Isobutane; Poly dimethylsiloxane; Water	Gycol Ether - Tire
	Misty Detailing & Dressing Spray	Hexane; Poly Dimethylsiloxane; Petroleum Distillates; Isobutane- Propane propellant	Hexane- Tire
	Mirachem 500 Foaming Aerosol	Aqueous with propane-isobutane propellants	Aqueous 1

Each product formulation claimed to meet the necessary requirement for the particular soil removal. Additionally, all the products were found to be non-corrosive with pH values ranging from 7.3 to 10. Three of the products provided one-step cleaning that resulted in a shiny tire. The last product did not specify if the process was a one-step process or if the tire would be shiny. The results for the performance comparison gathered from vendor information are listed in the Table 5.4.3 G.

Table 5.4.3 G: Tire Cleaning Performance Comparison

Product	Oil, grease, dirt	Shine	One Step	Non-corrosive -pH
Glycol Ether - Tire	Y	Y	Y	Y - 9-10
Hexane- Tire	Y	Y	Y	Y - 9.4-9.8
Glycol Ether - Tire	Y	Y	Y	Y - 7.3-8.3
Aqueous 1	Y			Y

Y = Yes, meets criteria according to manufacturer's claims

N = No, not expected to meet criteria

Blank = no information available from literature

Financial Assessment

A comparison on the purchase cost for alternative aerosol cleaners was conducted using data collected from various distributors of the aerosol products. Whenever possible, the price for one case of product was used. Normalizing the volume of the case was necessary as many of the products were available in different volumes. If more detailed information on performance were available, costs could also be normalized for amount of product required to do one job.

Brake Cleaning

The Heptane-Brake and the Aqueous 1 products had comparable costs. The Toluene-Brake product had the highest cost per ounce. This upfront purchase cost does not address usage rates. Some products may work more efficiently than others, requiring less material to clean the desired parts. This would bring the overall operating costs down. Typical costs for a PCE-based cleaning product are approximately $4/can or about $0.25/oz. Three of the four products were comparable to this purchase price and are listed in the Table 5.4.3 H.

Table 5.4.3 H: Cost Comparison for Brake Cleaners

Product	Purchase Price ($/oz)
Heptane-Brake	0.15
Hydrocarbon-Brake	0.28
Toluene-Brake	0.57
Aqueous 1-Brake	0.18

Engine Cleaner-External

Many of the alternative aerosol engine/parts cleaners had purchase costs that exceeded that for PCE-based products. Only two products had equal or lower prices. However, only two products were considerably higher than the PCE price. Depending upon efficacy of the alternatives, the higher costs could be offset by using less of a product per task. Purchase costs for engine cleaners are listed by product in Table 5.4.3 I.

Table 5.4.3 I: Cost Comparison for Engine Cleaner-External

Product	Purchase Price ($/oz)
Petroleum 1-Engine	No Data
Butoxyethanol-Engine	0.36
Terpene 1-Engine	0.43
Terpene 1-Engine	0.63
Aqueous 2	0.25
Aqueous 1	0.18
Aqueous 3	0.33

Engine Cleaner-Internal

Due to the cleaning requirements for carburetor and air intake cleaning, the purchase cost for the alternatives are much higher than the PCE based products. The prices are more than twice the cost of the $0.25/oz average for PCE aerosol cleaners. The costs for two of the three alternatives are listed in the Table 5.4.3 J.

Table 5.4.3 J: Cost Comparison for Engine Cleaner Internal

Product	Purchase Price ($/oz)
Toluene-Engine	No Data
Petroleum 2-Engine	0.59
Xylene-Engine	0.53

Tire Cleaner

Alternatives for tire cleaners were found to be similar to the cost of PCE ($0.25/oz). For the three products that data were available for, all three were equal to or less expensive than PCE (assuming 100% PCE in the reference product). Many of these products are foaming products. Table 5.4.3 K lists the costs.

Table 5.4.3 K: Cost Comparison for Tire Cleaners

Product	Purchase Price ($/oz)
Silicone-Tire	0.25
Glycol Ether-Tire	No Data
Hexane-Tire	0.20
Aqueous 1	0.18

Environmental Assessment

Several key parameters were reviewed to determine the potential impact of aerosol cleaning solvents in the environment. Human health effects will be discussed separately in the following section. Further information on environmental and health parameters and levels of concern are included in Appendix A; detailed data for automotive aerosol alternative chemistries are included in Appendix D.3. Initially, all products and their ingredients, including the current solvent, were analyzed using the EPA PBT profiler to determine persistence and bioaccumulation potentials.

Brake Cleaning

The constituents for each brake cleaner were not persistent in water. Each constituent had a half-life less than that for PCE (60 days). Soil half-lives were also lower than the PCE level for all components except one. The Hydrocarbon-Brake cleaner had one component, C9-C12 hydrocarbon, with a soil half-life listed as less than 180 days which persistence in soil. PCE had a soil half-life of 120 days, also in the considered persistent.

For sediment persistence, each component was lower then the PCE half-life of 540 days. All values for the alternatives were less than the 180 day limit for very persistent. Most of the listed alternatives had half-lives of approximately 140 days, indicating that they are persistent. There were some components for which a half-life could not be established.

Air persistence resulted in the most concern for half-life values. Only two components of one product, Hydrocarbon-Brake cleaner, were below the persistence level of 2 days. All other components and PCE were above this value. The air persistence is of concern as many of the components will end up in this medium due to the aerosol delivery system.

According to the MSDS for PCE, the solvent is considered to be toxic to fish. The only constituent in the alternatives that was of moderate concern for chronic fish toxicity was the heptane in the Heptane-Brake; its value was also close to the 0.1 mg/l limit for high level of concern.

PCE, toluene and methanol were all hazardous air pollutants on the NESHAP list. However, neither PCE nor any of the alternative products contained any chemical listed as ozone depleting or a greenhouse gas.

Engine Cleaner

Several of the constituents of the engine cleaners could not be assessed using the PBT Profiler because they are mixtures of chemicals within a particular chemical classification. This was the case for some petroleum distillates and soy-based products. For the remaining chemicals, the water and soil half-lives were low. The sediment half-life values were in the persistent range with most products having a 140 day half-life. Air half lives were mixed with some chemicals having low residence time in air, less than two days and others having longer times. Most formulations had at least one chemical with half-life greater than two days, indicating persistence in air.

Only d-limonene, found in Terpene 1-Engine and Terpene 2-Engine, was considered bioaccumulative. D-limonene had a BCF of 4770, which is close to the EPA threshold of 5000 for very bioaccumulative.

Two components, d-limonene, found in Terpene 1-Engine and Terpene 2-Engine, and nonyl phenol ethoxylate, found in the Butoxyethanol-Engine, had ChV values that would classify these chemicals as having chronic fish toxicity. D-limonene had value of 0.045mg/l, about half the established level of 0.1 mg/L. NPE had about one fifth of the 0.1mg/L level

No external alternative engine cleaning products contained chemicals that were hazardous air pollutants on the NESHAP list. However, the internal alternative cleaning products had some components that were hazardous air pollutants. These chemicals were xylene, toluene and methanol. No alternatives contained chemicals that would be classified as ozone depleting chemicals or greenhouse gases.

Tire Cleaner

Both water and soil persistence for the alternative constituents are below the 60 day half-life signifying that they are not persistent. Sediment persistence values were all lower than the 180 day limit for very persistent but were greater than the 60 day half-life. Air persistence resulted in the greatest number of constituents exceeding the persistent levels.

PCE is not considered to be bioaccumulative. Alternatives contain constituents that are both higher and lower than PCE, none of which exceed the EPA criteria for bioaccumulative.

Only Hexane-Tire contained a chemical, a petroleum distillate, with high concern for chronic fish toxicity with a ChV value of 0.056 mg/L. Several constituents had values greater than the 0.1mg/L but less than 10, indicating moderate concern for chronic fish toxicity.

PCE and hexane (in Hexane-Tire) were the only two products to be listed as hazardous air pollutants under NESHAP. No products contained ozone depleting chemicals or greenhouse gases.

Human Health Assessment

Acute Effects

Brake Cleaning

The assessed alternative brake cleaners did not contain any component that had a PEL lower than PCE. PEL's for constituents in alternatives ranged from 100 to 5000 ppm.

According to the NIOSH Pocket Guide to Chemical Hazards PCE can irritate the skin, the eyes and the respiratory tract. When possible, the alternative's potential to cause irritation was based on the product as a whole. Three of the four brake cleaners were found to irritate the skin, the eyes and the respiratory tract. The one alternative that was considered to be non-irritating was the Aqueous 1 product.

The use of n-hexane in brake cleaners reportedly can result in incidences of numbness of fingers and arms among users (HESIS 2001; CDC 2001). The HESIS Health Advisory Alert on n-hexane (CAS# 110-54-3) further states the chemical can enter the body when spray in the air is breathed in or comes in contact with skin. Exposure of long durations (months) can cause damage to nerves of the extremities called peripheral neuropathy. Symptoms of this condition can be numbness or tingling in the feet, legs and hands, a reduced sense of touch, pain, vibration or temperature and muscles may weaken in the legs, feet and hands. Symptoms have been seen to gradually improve when exposure ceases, but may last for months or be permanent. Short term exposures of n-hexane may produce headaches, dizziness, and loss of appetite or drowsiness but seem to improve a few hours after exposure ceases.

The HESIS Health Alert further states that workers exposed to air concentrations slightly over the workplace PEL of 50 ppm can suffer nerve damage.

Engine Cleaner

There was a wide range of PELs for the different constituents of the alternative aerosol engine cleaners. Therefore, for each engine cleaning product the constituent with the lowest PEL, REL or TLV was selected for comparison to PCE. Two external products (Petroleum 1-Engine and Butoxyethanol-Engine) each contained the component, 2-butoxyethanol, that had a PEL and TLV lower than those for PCE. The vapor pressure of 2-butoxyethanol is lower than PCE, so it is less likely to evaporate into the air than PCE. Depending on the percent of PCE and 2-butoxyethanol in the respective products, and their efficiency (how much product you need to clean effectively), this could result in lower exposures to 2-butoxyethanol. The internal engine alternatives had a PEL equal to PCE and a TLV that was greater than that for PCE. Table 5.4.3L lists the lowest values for each alternative aerosol product.

Table 5.4.3 L: Exposure Limits

	PEL (ppm)	REL (ppm)	TLV (ppm)
PCE	100		25
External			
Petroleum 1-Engine	50	5	20
Butoxyethanol-Engine	50	5	20
Terpene 1-Engine	1000	1000	
Terpene 1-Engine			
Internal			
Toluene-Engine	100	100	50
Petroleum 2-Engine			
Xylene-Engine	100	100	50

Most of the alternative products posed the same hazards as PCE for the skin, the eyes and the respiratory tract.

Tire Cleaner

Many of the alternative tire aerosol cleaning formulations did not have PELs for their constituents. For the chemicals with PEL's, only one was lower than the 100 ppm currently established for PCE. This component diethylene glycol monoethyl ether, (Glycol Ether-Tire) had a PEL of 50 ppm. When comparing the TLV's for the alternatives, all of the listed values were safer than the 25 ppm value set for PCE.

Each product contained at least one component that would either cause irritation to the skin, eyes and the respiratory tract. When looking at each product as a whole, the only alternative considered to be non-irritating was Aqueous 1.

Chronic Effects

Long term hazards include mutagenicity, carcinogenicity and reproductive and developmental toxicity. The EPA has classified PCE as reasonably anticipated to be a human carcinogen and IARC lists the solvent as a 2A probable. PCE can affect the eyes, skin, respiratory system, liver, kidneys and the central nervous system.

Brake Cleaner

Toluene was the only alternative constituent with listed chronic effects. This chemical was found in the Toluene-Brake. Toluene is listed as a developmental toxin under California's Proposition 65 and adversely affects the central nervous system.

The alternatives contain at least one chemical constituent that can affect the skin, respiratory system and central nervous system. Three of the products contain components that also affect the eyes. Aqueous 1 was the only product that did not contain such an eye hazard. Toluene-Brake also could affect the lungs, liver, kidney and the gastrointestinal tract.

Engine Cleaner

Toluene used in engine cleaners have adverse chronic effects (see discussion for brake cleaners above). Several studies also have shown reproductive effects from glycol ether exposure.

Each of the alternatives contains at least one chemical that can affect the skin, respiratory tract and the kidneys. In additional all but Terpene 1-Engine contained a component that can affect the eyes. Petroleum 2-Engine and Terpene 2-Engine do not contain chemicals that would affect the central nervous system.

Tire Cleaner

No constituents of the aerosol tire cleaners were recorded as being mutagens or carcinogens. One component, poly dimethylsiloxane, found in two products (Glycol Ether-Tire and Hexane-Tire) has been shown in studies to cause reproductive or developmental effects. In addition, one product formulation, Glycol Ether-Tire, had reproduction or development effects listed on the MSDS.

Other Hazards: Flammability and Flash Point

PCE is considered to be non flammable and has no flash point. Based on the NFPA rating system PCE has a zero fire hazard.

Brake Cleaning

Aqueous 1 was the only alternative brake cleaner with a flash point greater than 100°C and an NFPA rating of one for fire. The other products (Heptane-Brake, Hydrocarbon-Brake, Toluene-Brake) had an NFPA fire rating of three and flash points less than 0° C. These products are considered flammable.

Engine Cleaner

The Butoxyethanol-Engine product had an NFPA rating of 2 and flashpoint of 64° C. Likewise, Petroleum 2-Engine had an NFPA rating of 2 and a flashpoint of 60° C. The Terpene 1-Engine based cleaner had an NFPA rating of 4 and flashpoint of -10° C. Similarly, Xylene-Engine cleaner had an NFPA rating of 4 and a flash point of -97° C. Although the Toluene-Engine did not have an NFPA rating for the product as a whole, three of the four components had NFPA ratings of three for fire. The flashpoints for these three components were less than 30° C. One alternative, Petroleum 1-Engine, did not have enough information to characterize the flashpoint.

Tire Cleaner

Two products, Silicone-Tire and Aqueous 1, had flash points greater than 93.3° C and NFPA ratings of one for flammability. Glycol Ether-Tire did not list a flash point for the complete formulation and had an NFPA rating of two for fire. The remaining product, Hexane-Tire, did not have either a flash point or NFPA rating listed for the complete product.

Other Hazards: Reactivity

Brake Cleaning

All of the aerosol brake cleaning solvents had an NFPA Reactivity rating of zero and would be considered to not cause a worker risk in this category.

Engine Cleaner

The Terpene 1-Engine based cleaner and the Petroleum 2-Engine product both had an NFPA rating of one for reactivity which would result in the product becoming unstable if heated.

Tire Cleaner

Only one constituent, Dimethyl Ether in the Glycol Ether-Tire product had an NFPA rating of one for reactivity. All other components in this formulation had an NFPA rating of zero.

Other Hazards: Corrosivity

Corrosivity was measured using pH values. Products with a pH less than 2 and greater than 12 would be considered to be corrosive. Products with no pH, such as PCE, would not be applicable to this measurement of corrosivity.

None of the alternative products for the three automotive aerosol applications were considered to be corrosive.

Summary of Automotive Aerosol Alternatives

Effectiveness of the alternatives and information regarding constituents was based on information supplied by manufacturers. No independent testing has been conducted to verify and compare the performance of these alternatives to PCE based products.

Brake Cleaning

More information is needed on the control of fibrous particles as a criterion. One product claims to limit the fibers from becoming airborne, for the others it was inferred or unknown. Depending on the nature of the airborne fibers, they could pose a serious health risk to the worker due to the body's difficulty in clearing these particles from the lung.

The alternatives are comparable in purchase price. Only one product (Toluene-Brake) had higher cost than the current cost for PCE-based products.

The assessed alternatives had lower environmental persistence. Neither PCE nor the alternatives exceed the EPA limit for being considered bioaccumulative. The worker exposure review showed that the alternatives may be safer for the user than PCE based cleaners. The alternatives also had the same reactivity and corrosivity levels as the traditional cleaner. The Heptane Brake and the Hydrocarbon Brake have flammability concerns. Only one product, Toluene-Brake had similar mutagenicity and reproductive or developmental toxicity levels as PCE.

The summary for brake cleaning alternatives is found in Table 5.4.3 M. For most indicators, the alternatives appear to offer an improved environmental, health and safety profile over PCE. All except the Aqueous 1 product are flammable, however, and introduce a new hazard to the work environment.

Table 5.4.3 M: Assessment Summary for Brake Cleaning Alternatives

Assessment Criteria		PCE reference	Heptane-Brake	Hydrocarbon-Brake	Toluene-Brake	Aqueous 1
Technical Criteria	Cleaning	Effective	=	=	=	=
	Fiber control	Unknown	-	?	?	?
	Drying	Quick	?	=	?	-
	Residue	None	?	=	=	-
	Flammable	Non	-	-	=	=
Financial Criteria	Purchase	$0.25/oz	+	=	-	+
Environmental Criteria	Water	60 days	+	+	+	+
	Soil	120 days	+	=	+	+
	Sediment	540 days	+	+	+	+
	Air	98 days	=	+	=	+
	BCF	83	-	-	+	+
Human Health Criteria	Exposure limits	100 ppm; 25 TLV	+	+	+	+
	Dermal/Occular/Respiratory	Irritant	+	=	=	+
	Mutagenicity	No	=	=	-	=
	Carcinogenicity	2A	+	+	+	+
	Reproductive or Developmental Toxicity	No	=	=	-	=
Safety Criteria	Flammability	Nonflammable	-	-	-	+
	Reactivity	Non reactive	=	=	=	=
	Corrosivity	Non corrosive	=	=	=	=

Comparison Key + Better = Similar - Worse ? Unknown

Engine Cleaning – External

One important criterion for engine cleaning was the ability of the cleaner to cling to a vertical surface. Half of the evaluated products appeared to meet this criterion. Most of the products had comparable flash points to PCE. Only two products could be confirmed to leave no residue behind after cleaning was completed and only one product had a similar non-VOC status to PCE.

Four of the alternatives cost more than PCE-based products. The two aerosol aqueous based alternatives were approximately the same or less expensive than PCE was. An industry expert also stated that for whole engine cleaning and degreasing a non aerosolized aqueous parts and engine cleaning system can work as well as an aerosolized solvent cleaner and may prove less expensive due to the amount of cleaner needed to clean an entire engine.

Nearly all of the evaluated products had improved environmental persistence profiles. One product had higher air persistence and two had higher BCF levels. The aqueous based products could not be assessed for the worker exposure profile as there was not enough constituent information. The only listed components were for the propellants. However, typically this class of products would have a better profile than solvent based products for worker health and safety. In all other cases, the alternatives had fewer hazards for the worker than PCE-based products.

It should be noted again that PCE-based cleaners have not been widely used for general engine cleaning due to the higher evaporation rate of the PCE cleaners but that they have been used for cleaning parts of the engine that need to be removed and repaired. The summary table for engine (external) cleaning alternatives is found in Table 5.4.3 N and shows that the alternatives appear to be less toxic to the environment and be less persistent and bioaccumulative. For human health effects the alternatives seem to be of less concern for chronic health hazards of carcinogenicity, mutenagenicity and reproductive and developmental hazards. The two products that contain 2-butoxyethanol are a concern for worker exposure. The exposure limits for that constituent are lower than for straight PCE.

It should also be noted that the possible synergistic effect of chemical mixtures has not been evaluated in this assessment.

Table 5.4.3 N: Assessment Summary for Alternatives Engine Cleaning (External) Aerosols

Assessment Criteria		PCE reference	Petroleum 1-Engine	Butoxyethanol-Engine	Terpene 1-Engine	Terpene 2-Engine	Aqueous 2	Aqueous 1
Technical Criteria	Cleaning	Effective	=	=	=	=	=	=
	Cling to surface	Unknown	+	?	?	?	+	+
	Residue	None	?	+	?	?	+	-
	Flash Point	None	=	=	-	=	=	=
Financial Criteria	Purchase	$0.25/oz	-	-	-	-	=	+
Environmental Criteria	Water	60 days	+	+	+	+	+	+
	Soil	120 days	+	+	+	+	+	+
	Sediment	540 days	+	+	+	+	+	+
	Air	98 days	+	-	+	+	+	+
	BCF	83	+	+	-	-	+	+
Human Health Criteria	Exposure limits	100 ppm; 25 TLV	-	-	+	?	?	+
	D/O/R	Irritant	=	=	=	=	?	+
	Mutagenicity	No	=	+	+	+	?	+
	Carcinogenicity	2A	+	+	+	+	?	+
	Rep/Develop	No	+	+	+	+	?	+
Safety Criteria	Flammability	Nonflammable	-	-	-	=	?	+
	Reactivity	Non reactive	=	=	=	=	?	=
	Corrosivity	Non corrosive	=	=	=	=	?	=

Comparison Key + Better = Similar - Worse ? Unknown

Engine Cleaning - Internal

Only one product, Toluene-Engine, was assumed to meet the fuel additive requirement as this product was specifically designed to clean carburetors. The other two alternatives were more generalized cleaners and the same assumption could not be made for them.

Costs were again higher for two of the products reviewed (Petroleum 2-Engine and Xylene-Engine) and unknown for the third (Toluene-Engine).

From an environmental standpoint, the alternatives had lower environmental persistence. Only one of the formulations had a BCF that was worse than the PCE value. The alternatives were comparable or better than PCE for most human health effects. Each of the alternatives had some level of concern regarding flammability whereas PCE is non flammable. The summary table for engine (internal) cleaning alternatives is found in Table 5.4.3 O and the same issues seen for external engine cleaners and the other automotive aerosols should be considered for this use as well.

Table 5.4.3 O: Assessment Summary for Alternative Automotive Engine Cleaning (Internal) Aerosols

Assessment Criteria		PCE reference	Toluene-Engine	Petroleum 2-Engine	Xylene - Engine
Technical Criteria	Cleaning	Effective	=	=	=
	Fuel Additive	Unknown	+	?	?
Financial Criteria	Purchase	$0.25/oz	?	-	-
Environmental Criteria	Water	60 days	+	+	+
	Soil	120 days	+	+	+
	Sediment	540 days	+	+	+
	Air	98 days	+	+	+
	BCF	83	+	-	+
Human Health Criteria	Exposure limits	100 ppm; 25 TLV	=	?	=
	D/O/R	Irritant	=	=	=
	Mutagenicity	No	+	+	+
	Carcinogenicity	2A	+	+	+
	Rep/Develop	No	+	+	+
Safety Criteria	Flammability	Nonflammable	-	-	-
	Reactivity	Non reactive	=	=	=
	Corrosivity	Non corrosive	=	=	=

Comparison Key + Better = Similar - Worse ? Unknown

Tire Cleaning

Most of the alternatives met the desired criteria for a tire cleaner. Only one product (Aqueous 1) did not specify whether it created a shine on the tire or whether it was a one-step process. This product was more of a general cleaning product that may be effective for tire cleaning. The identified alternatives cost approximately the same (Silicone-Tire or less Hexane-Tire and Aqueous 1) as PCE-based products. Only one product (Glycol Ether-Tire) did not have cost information.

Environmental persistence for each alternative was lower for water, soil, sediment and air. The BCF for two products (Glycol Ether-Tire and Hexane-Tire) was greater than PCE. Only one product (Glycol Ether-Tire) had a higher PEL. All other worker exposure data were equal to or better than a

PCE based product. Flammability concerns were found for three of the four alternatives. The summary table for tire cleaning alternatives is found in the Table 5.4.3 P.

Table 5.4.3 P: Assessment Summary for Alternatives for Automotive Tire Cleaning Aerosols

Assessment Criteria		PCE reference	Silicone-Tire	Glycol Ether-Tire	Hexane-Tire	Aqueous 1
Technical Criteria	Cleaning	Effective	=	=	=	=
	Shine	Yes	+	+	+	?
	One Step	Yes	+	+	+	?
	Non-corrosive	Yes	=	=	=	=
Financial Criteria	Purchase	$0.25/oz	=	?	+	+
Environmental Criteria	Water	60 days	+	+	+	+
	Soil	120 days	+	+	+	+
	Sediment	540 days	+	+	+	+
	Air	98 days	+	+	+	+
	BCF	83	+	-	-	+
Human Health Criteria	Exposure limits	100 ppm; 25 TLV	+	-	+	+
	D/O/R	Irritant	=	=	=	+
	Mutagenicity	No	=	=	=	=
	Carcinogenicity	2A	+	+	+	+
	Rep/Develop	No	-	=	=	=
Safety Criteria	Flammability	Nonflammable	-	-	-	+
	Reactivity	Non reactive	-	=	=	=
	Corrosivity	Non corrosive	=	=	=	=

Comparison Key + Better = Similar - Worse ? Unknown

Emerging Aerosol Cleaning Alternatives

Recently a study was conducted by Institute for Research and Technical Assistance (IRTA) for California's Department of Health Services Hazard Evaluation System & Information Service (HESIS) to identify and test alternative safer water-based aerosol cleaning products. The focus was on developing and testing alternative aerosol cleaners for four categories of automotive cleaning (HESIS 2004). In addition to the water based products, the project including developing, testing and demonstrating low-VOC, low toxicity soy/acetone based cleaners as potential alternatives.

From field testing conducted by various end users, the alternatives performed adequately and, in some cases, very well. The VOC content of the alternative cleaners ranged from zero to 10% using hydrocarbons as the propellant. If carbon dioxide could be used as a propellant for the water-based cleaners, the VOC content of the alternative products would be near-zero. The alternative products developed and tested during this project are lower in toxicity than most products currently used in aerosol automotive cleaning applications (HESIS 2004).

Despite the success of many of the products, IRTA determined from their testing that the water based formulations foamed when they were packaged into an aerosol delivery. As described previously, foaming is considered a benefit for some uses but can cause problems in processes that require fast drying such as brake cleaning.

Although it was not originally part of the project plan, IRTA included an evaluation of alternative propellants in an attempt to find one that would not contribute to smog formation. The most common propellants in automotive aerosols are hydrocarbon-based. The hydrocarbons are VOCs that lead to the creation of smog. Additionally, during the testing process, IRTA found that the alternative propellants could improve the overall performance of the alternative products. When the soy/acetone products for carburetor and fuel injection system cleaning were packaged with both hydrocarbon and carbon dioxide propellants the IRTA found that the carbon dioxide propelled products had a better delivery and cleaning efficiency (HESIS 2004).

The two delivery mechanisms included carbon dioxide and nitrogen. As mentioned, the carbon dioxide propellant improved delivery and efficiency with certain formulations. However, a major disadvantage of carbon dioxide arises when it is used with highly alkaline water-based cleaners. It can react with the alkaline components forming carbonic acid which can lead to corrosion of the can.

Nitrogen was considered as a propellant because it is not classified as a VOC and it has a very low cost. Two problems have been observed with nitrogen propellants. First, some packagers claim it loses pressure as the product is expelled from the aerosol. Second, other packagers claim that it has lower pressure on a continuous basis as the product is expelled.

One possible solution to the loss of pressure during usage would be to utilize a rechargeable system. EnviroCaddie LLC has a unit designed for spraying brake cleaners, penetrants and choke cleaners. The device is designed to be refillable & rechargeable, thus eliminating this drawback. The reusability of the container would eliminate the need for aerosol can disposal. According to the manufacturer, any product that can be sprayed from an aerosol container also could be sprayed from the EnviroCaddie equipment.

The company offers an array of cleaning products that from recognized manufacturers (Dynatex; CRC; Castle) which can be used effectively in the EnviroCaddie II. They will also consider other products and formulations on an individual basis (ENVIROCaddie LLC).

5.5 Summary and Conclusions

Perchloroethylene, or PCE, is a non-flammable, man-made chlorinated hydrocarbon with the chemical formula C_2Cl_4. It is used primarily as a solvent in dry cleaning, industrial degreasing and as a chemical intermediate.

Exposure to PCE can be as a result of environmental contamination, presence in consumer products or occupational sources. PCE levels in the environment tend to be higher in urban and industrial areas. The most prevalent route of exposure to PCE is by inhalation and it is readily absorbed into blood through the lungs. Other exposure routes of concern are oral via drinking water or contaminated food. Dermal exposure is generally considered a minor route of exposure but direct skin exposure to PCE in the liquid form can result in irritation and blistering.

Target organs for PCE are the central nervous system, kidneys and the liver. Some studies suggest that frequent over exposure to some organic solvents over months or years may cause lasting and possibly permanent central nervous system effects. IARC lists PCE as Group 2A, "probably carcinogenic to humans".

The three PCE uses assessed in this study are dry cleaning, vapor degreasing and automotive aerosol cleaners. These uses were chosen because of their importance to Massachusetts and their potential for worker and consumer exposure.

5.5.1 Dry Cleaning

Complete alternatives assessments were performed for five alternatives to PCE, *i.e*, hydrocarbons (HC), volatile methyl siloxanes (VMS), substituted aliphatic glycol ethers (SGE), wet cleaning, and liquid carbon dioxide (CO_2). A specific formulation was selected from each of the first four categories for detailed analysis; these assessments should be considered to be representative of each category. The first four alternatives are commercially available in Massachusetts, and interviews with users find that, in general, technical and economic performance approaches that of PCE. No commercial CO_2 facilities were identified in Massachusetts, although there are facilities in other states.

In general, the EH&S impacts of the solvent-based alternatives are less well-understood than those of PCE, with an absence of in-depth toxicological studies in the peer-reviewed literature; overall, however, they appear to represent an improvement over PCE. There is one major exception - the three solvent-based cleaners, HC, VMS and SGE, are combustible where PCE is not. Importantly, none of the alternatives are suspected or confirmed human carcinogens, although this may be due to the lack of any studies being performed as reflected in the absence of published studies in the peer-reviewed literature.

5.5.2 Vapor Degreasing

The alternatives assessment was limited to drop-in replacements to PCE; aqueous cleaning systems were not included since the TURI SSL has already documented the advantages and disadvantages of this approach. A product based on n-propyl bromide (nPB), a product based on VMS, and two hydrochlorofluorocarbons (HCFCs) were selected for the alternatives assessment.

Soil removal testing performed at the TURI SSL as part of another study found that all four alternatives were as effective as PCE in removing oil-based soils. The alternative cleaners had higher vapor pressures than PCE, which will contribute to product loss through evaporation. On the other hand, the alternatives all had lower surface tensions than PCE, which should enhance their ability to clean complex parts.

The financial assessment found that all of the alternatives were considerably more expensive to purchase than PCE, although other operating costs such as energy use, waste solvent handling costs, and solvent lifetime would tend to reduce the overall cost differential. On the other hand, all of the alternative solvents are more volatile than PCE, which could increase costs due to greater evaporative losses.

All of the alternatives have potentially significant environmental and occupational health and safety impacts. The HCFC products have significant adverse environmental impacts, including persistence and global warming potential, but should be somewhat less toxic than PCE. There are significant concerns about the toxicity of nPB; it is a neurotoxin, and its carcinogenicity is now under study. The ACGIH TLV for nPB is 10 ppm, well below the PCE TLV of 25 ppm. VMSs can cause dizziness, disorientation, and shortness of breath, but at relatively high exposure levels; the manufacturer's recommended exposure limit is 200 ppm.

All of the alternatives have higher vapor pressures than PCE, which will lead to greater evaporation and the potential for more vapors to escape from the degreaser; this will increase the potential for worker exposure, and may cause greater fugitive emissions than with PCE. A significant safety hazard is presented by the particular VMS studied, which is highly flammable with a very low flash point. Its use in a vapor degreaser would present a significant fire and explosion hazard.

5.5.3 Aerosol Automotive Cleaning

Many alternative automotive cleaning products are available commercially, so a large number of alternatives were evaluated. Full alternatives assessments were performed on four brake cleaning alternatives, seven external engine cleaning alternatives, three internal engine cleaning alternatives, and four tire cleaning alternatives.

It is difficult to assess the likely technical performance of any of the alternatives, since actual test data are not available. Experts indicated that the alternative solvent-based cleaners are likely to perform as well as PCE-based cleaners, but that aerosol-type aqueous-based cleaners may require more mechanical agitation (*i.e.,* hand-scrubbing) to achieve equivalent results. Cost information is also difficult to assess. Some alternative products were more expensive per ounce than their equivalent PCE product, and some were less expensive per ounce. The actual cost *per use* may be quite different, however, since more or less of the different products may be required to obtain equivalent cleaning ability.

Many of the alternative cleaners had the potential for significant environmental impact upon release; the medium of most concern is air, since these products are used as aerosol sprays. Most of the alternative products had ingredients with atmospheric half-lives exceeding two days, which is also the case for PCE; this puts them in the persistent category.

With regard to human toxicity, the products containing n-hexane, toluene, and two glycol ethers, 2-butoxyethanol and diethylene glycol monomethyl ether (DGME), will be of equal or more concern to those products containing PCE. The aqueous-based products will have lower human health concerns than any of the solvent-based products.

Flammability is an issue for many of the alternatives. Most of the solvent-based cleaners are highly flammable, and great care must be taken in their use – especially around hot engines. PCE is nonflammable, as are the aqueous-based cleaners, so these alternatives are preferable with regard to fire potential.

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Chapter 6. Hexavalent Chromium

Five Chemicals Alternatives Assessment Study

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6.1 Overview

6.1.1 Characteristics of Hexavalent Chromium

Chromium is a metallic element. It is not found in nature in its elemental form, but rather in chromite ore ($FeCr_2O_4$) or, less frequently, the mineral crocoite (PbCr) (Barceloux 1999). Chromium used in industry is derived from chromite ore, the majority of which is imported from South Africa and Kazakhstan. No chromite mines currently exist in the United States (Barnhart 1997).

There are several oxidation (or valence) states of chromium, each with its own chemical characteristics. The most common forms are trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). Trivalent chromium compounds can be can be either naturally occurring or a by-product of industry, while elemental chromium and the hexavalent compounds nearly always result from industrial activity. The most common hexavalent chromium compounds are chromates and chromic acid (Table 6.1 A) (Page, Loar 1991).

Trivalent chromium is the more stable form, and trivalent chromium compounds generally have low solubility in water and low reactivity (Barnhart 1997). Most hexavalent chromium compounds are soluble in water, and are strong oxidizers. Both trivalent and hexavalent compounds are denser than water. Under low pH conditions and in the presence of organic matter, some hexavalent chromium compounds may reduce to the trivalent form. Conversely, Cr(III) may convert to Cr(VI) in high pH conditions, or in the presence of free chlorine in neutral pH water that has little organic material (Independent Environmental Technical Evaluation Group (IETEG) 2005; Clifford, Dennis 1988).

Table 6.1 A: Hexavalent Chromium Compounds Nomenclature

Name	Synonyms	Chemical Formula	CAS #
Ammonium dichromate	Dichromic acid,,diammonium salt Ammonium bichromate	$(NH_4)Cr_2O_7$	7789-09-5
Barium chromate	Chromic acid, barium salt Barium chromate oxide CI Pigment Yellow 31 Lemon chrome	$BaCrO_4$	10294-40-3
Calcium chromate	Chromic acid, calcium salt Calcium monochromate Calcium chromium oxide Calcium chrome yellow	$CaCrO_4$	13765-19-0
Chromium trioxide	Chromic acid Chromium anhydride Chromium oxide	CrO_3	1333-82-0
Lead chromate	Chromic acid, lead salt Chrome green Chrome yellow	$PbCrO_4$	7758-97-6
Potassium chlorochromate	Peligot's salt Chlorochromic acid, potassium salt	$KCrO_3Cl$	16037-50-6
Potassium chromate	Chromic acid, dipotassium salt Tarapacaite	K_2CrO_4	7789-00-6
Potassium dichromate	Chromic acid, dipotassium salt Bipotassium chromate	K_2CrO_7	7778-50-9
Silver chromate	Chromic acid, disilver salt	Ag_2CrO_4	7784-01-2
Sodium chromate	Chromic acid, disodium salt Chromium disodium oxide Disodium chromate	Na_2CrO_4	7775-11-3
Sodium chromate, dihydrate	Chromic acid disodium salt; dihydrate Sodium bichromate Sodium dichromate, dihydrate	$NaCr_2O_7{*}2H_2O$	7789-12-0
Strontium chromate	Chromic acid, strontium salt Deep lemon yellow	$SrCrO_4$	7789-06-2
Zinc chromate	Chromic acid, zinc salt Buttercup yellow Chromium zinc oxide	$ZnCrO_4$	13530-65-9
Agency for Toxic Substances and Disease Registry (ATSDR) 2000, International Agency for Research on Cancer (IARC) 1990, Page, Loar 1991			

Table 6.1B presents chemical and physical characteristics of hexavalent chromium compounds.

Table 6.1 B: Hexavalent Chromium Chemical/Physical Characteristics

Name	Melting/boiling point	Solubility in water (g/100 cm³)	Density (g/cm³)	Appearance
Ammonium dichromate	Decomposes at 170° C	30.8 @ 15° C	2.155 @ 25° C	Red-orange crystals
Barium chromate	Decomposes	0.00034 @ 16° C	4.498 @ 25° C	Black-green crystals

Table 6.1 B: Hexavalent Chromium Chemical/Physical Characteristics

Name	Melting/boiling point	Solubility in water (g/100 cm^{3})	Density (g/cm^{3})	Appearance
Calcium chromate	No data	2.23	2.89 (no temp specified)	Yellow prisms
Chromium trioxide	197° C/decomposes	61.7 @ 0° C	2.7 @ 25° C	Dark red crystals
Lead chromate	844° C/no data	5.8	6.12 @ 15° C	Yellow, orange or red crystals
Potassium chlorochromate	Decomposes	Decomposes in water	2.497 @ 39° C	Orange needles or purplish crystals
Potassium chromate	975° C/no data	62.9 @ 20° C	2.732 @ 18° C	Orange-red crystals
Potassium dichromate	398 °C/decomposes at 500 °C	4.9 @ 0° C	2.676 @ 25° C	Orange-red crystals
Silver chromate	No data	0.014 @ 25° C	5.625 @ 25° C	Maroon crystals
Sodium chromate	792 °C/no data	87.3 @ 30° C	2.723 @ 25° C	Yellow crystals
Sodium chromate, dihydrate	356 °C/decomposes at 400 °C	230 @ 0° C	2.348 @ 25° C	Orange-red crystals
Strontium chromate	No data	0.12 @ 15° C	3.895 @ 15° C	Yellow crystals
Zinc chromate	No data	Insoluble	3.4 (temp not specified)	Lemon yellow prisms
ATSDR 2000, IARC 1990, Page, Loar 1991				

6.1.2 Health and Environmental Impacts

Hexavalent and trivalent chromium compounds differ in their health and environmental effects, with the hexavalent form being far more dangerous. Ingesting small to moderate amounts of trivalent chromium is essential to human metabolism, and there is no current evidence that Cr(III) is carcinogenic. In contrast, exposure to Cr(VI) is known to be a serious human health risk (Cohen, Costa 2000).

Acute (Short-Term) Health Effects

Short-term effects of hexavalent chromium exposure (for example, from chromic acid droplets or chromate dust) include eye irritation and respiratory irritation, sneezing, or sensitization; in high concentrations, acute inhalation can cause ulcers in the nasal septum. In sensitive individuals, inhalation of Cr(VI) can cause an asthma attack. If very small quantities are ingested the body converts it to the trivalent form in the stomach. In larger quantities or concentrations, however, ingestion of hexavalent chromium compounds can result in acute gastroenteritis, vertigo, gastrointestinal hemorrhage, convulsions, ulcers, kidney damage or failure, and liver damage or failure; approximately 1 g of potassium chromate is considered a lethal dose. Significant acute exposure of the skin to Cr(VI) can cause burns, liver damage or failure, kidney damage or failure, and anemia (ATSDR 2000).

Chronic (Long-Term) Health Effects

Long-term inhalation of hexavalent chromium is known to cause lung cancer (IARC 1990). It also can result in damage to the nasal mucous membrane, perforation of the nasal septum, and asthma. If inhaled through the mouth, it can cause periodontitis and gingivitis. Impacts of chronic skin exposure include dermatitis, hypersensitivity reactions, eczema, and kidney or liver damage. The characteristic lesions resulting from hexavalent chromium exposure are referred to as "chrome holes" or "chrome ulcers." Chronic eye exposure can result in conjunctivitis. (Drew et al. 2000).

Exposure Routes

Inhalation (of fumes or mist) and dermal contact with hexavalent chromium compounds used by workers in industrial operations are the primary exposure routes. Ingestion of large amounts most often is accidental or done with suicidal intentions. If soil is contaminated with Cr(VI), it is possible that it will be touched and/or swallowed (for example, by children playing in a contaminated area). In areas where there has been industrial pollution of groundwater, there is the potential for ingesting Cr(VI)-contaminated drinking water from groundwater wells. The family members of chromium workers also may be exposed inadvertently via contaminated work clothes (Pellerin et al. 2000).

Worker Health

Workers, rather than consumers, have the highest risk of adverse health effects from hexavalent chromium exposure. The industries with the greatest risk of occupational exposure to Cr(VI) are chrome electroplating[8], stainless steel welding, metal coating and painting, printing, textiles, leather tanning, wood preservation, and cement or masonry work. Inhalation risk may be from fumes (welding), mists or droplets (electroplating, spray painting.) Dermal exposure can result from contact with fluids, such as those used in electroplating, or materials containing Cr(VI), such as wet cement; smoking can increase the risks from Cr(VI) exposure. (OSHA, 2006)

For many years the OSHA PEL for hexavalent chromium compounds in workplace air was 52 $\mu g/m^3$ (ceiling concentration). That level was challenged by a variety of groups as being too high to adequately protect worker health, and OSHA proposed a rule (under a court-ordered deadline) that would lower the PEL to 1 $\mu g/m^3$ (time-weighted average) (U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) 2006). The final rule, issued on February 28, 2006, set the PEL at 5 $\mu g/m^3$ (time-weighted average). The NIOSH REL is 1 $\mu g/m^3$ (Pellerin et al. 2000). As a general rule, OSHA and NIOSH strongly recommend that all exposures to confirmed human carcinogens, such as hexavalent chromium, be reduced to the lowest possible level.

Public Health

Consumer exposure to hexavalent chromium most often is limited. Situations in which there may be non-worker exposure to Cr(VI) include contact with contaminated soil or ash at a waste disposal site, ingestion of contaminated well water or soil, inhalation of contaminated air near manufacturing operations involving chromium, contact with Cr(VI)-containing products (such as improperly tanned leather), inhalation of wear particles from brake linings or catalytic converters near highways (ATSDR 2000), or exposure from hobbyist uses (for example, gum bichromate photo processing or home electroplating.)

Environmental Hazards

There are both naturally occurring and anthropogenic sources of chromium compounds in the air, soil, and water. Natural sources include volcanic activity and the weathering of chromium-containing rock. Human activities resulting in the release of hexavalent chromium as a waste or by-product include fossil fuel combustion, steel production, chemical manufacturing, metal finishing and paint

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[8] A hexavalent chromium electroplating bath produces severe off gassing, resulting in the creation of a large amount of chromic acid mist at the surface of the plating tank.

manufacturing, ore refining, refractory brick production, cement production, leather tanning, pulp production, and wood preservation (Independent Environmental Technical Evaluation Group (IETEG) 2005).

Chromium in the air is in the form of particles or droplets, which may be transported by wind and/or deposited onto soil or water. The behavior of chromium compounds in soil and water is complex. Factors that determine whether the chromium is in trivalent or hexavalent form in different environmental media (air, soil, surface water, ground water) include pH, oxygen levels, temperature, and the presence of other chemicals and organic matter (Kotas, Stasicka 2000). Cr(VI) can leach out of soil into groundwater and migrate over time (IETEG 2005).

Hexavalent chromium's toxicity to aquatic organisms varies, depending on the species and the chemical characteristics of the water. Algae, saltwater polychaete worms, freshwater and marine crustaceans, rainbow trout, lake trout and some catfish species are relatively sensitive to Cr(VI). Ingestion of CR(VI) compounds by mammals can be lethal or can result in severe developmental effects, and ingestion by birds can cause deformities in embryos or reduced survival rates of chicks. In addition, the presence of Cr(VI) in irrigation water can kill some types of earthworms (Eisler 1986).

6.1.3 Use and Functionality

Chromium compounds have been used since the eighteenth century for a variety of industrial applications. The earliest uses for chromium compounds were as pigments, as mordants in textile dyeing, and in leather tanning. The use of chromium in stainless steel and refractory bricks became common in the early twentieth century. Electroplating, a key use of chromium, was invented in the 1920s (IETEG 2005).

Chromium can provide manufactured products with hardness, shininess, durability, color, corrosion resistance, heat resistance, and decay resistance. For example, decorative chrome plating produces a hard, shiny, durable surface coating on items such as school furniture. Jet turbine engine parts rely on hard chrome plating to resist corrosion, high temperatures, and wear. Chromium-based pigments are valued for their vivid colors and resistance to weathering; they are commonly used in traffic paints for those reasons. Anti-corrosion coatings containing chromium compounds are widely used in marine applications, where their resistance to salt spray and their "self-healing" properties are important. In addition, the biocidal properties of chromium compounds are key to their use in wood preservatives.

Uses in Products

The major application of chromium is in the production of alloys, primarily stainless steel; historically, this has amounted to 50-60% of total chromium use (Independent Environmental Technical Evaluation Group (IETEG 2005). Wood preservation, metal processing, leather tanning, and pigments are the main uses of chromium compounds.

Table 6.1 C: Uses of Hexavalent Chromium Compounds

Compound	Uses
Ammonium dichromate	Magnetic media, photo engraving, textile dyes, leather tanning
Barium chromate	Pigments, anti-corrosion coatings
Calcium chromate	Pigments, anti-corrosion coatings

Table 6.1 C: Uses of Hexavalent Chromium Compounds

Compound	Uses
Chromium trioxide	Chrome plating, stainless steel manufacture, fungicides, wood preservatives
Lead chromate	Pigments for paint, inks and plastics
Potassium chlorochromate	Photographic developing
Potassium chromate	Algaecides, fungicides, textile dyes
Potassium dichromate	Fungicides, wood preservatives, photographic engraving, pigments, textile dyes
Silver chromate	Catalyst, photographic media, conversion coatings
Sodium chromate	Fungicides, insecticides, miticides, wood preservatives, pigments, anti-corrosion coatings, textile dyes
Sodium chromate, dihydrate	Fungicides, insecticides
Strontium chromate	Paint manufacture, anti-corrosion coatings
Zinc chromate	Paint manufacture, anti-corrosion coatings
California Department of Health Services, Hazard Evaluation System and Information Service	

Uses for Chromium and Chromium Compounds in Massachusetts Manufacturing

Based on filings for 2003 under the Massachusetts Toxics Use Reduction Act (TURA), the companies using chromium and chromium compounds in the greatest quantity in Massachusetts are involved in wood preservation; manufacture of metal, metal finishing, and electroplating products; provision of electroplating services; production of paints and pigments; and manufacture of asphalt roofing shingle granules. Chromium also is generated as a by-product of several power plants.

Table 6.1 D: Use of Chromium and Chromium Compounds in Massachusetts
(includes all species of chromium)

Major Use Category	TURA Total Use (2003)	Pounds	Number of Filers
Wood Preservation	32 %	514,846	3
Metals Processing and Plating	24 %	391,598	4
Paints, Pigments, Dyes	21 %	347,199	7
Specialty and Metal Finishing Chemicals	12 %	200,233	3
Power Generation (by-product)	9 %	144,576	3
Photographic Chemicals	2 %	29,840	2
Totals:	**100 %**	**1,628,292**	**22**

6.2 Use Prioritization

Summary of Stakeholder Input

Because of the severity of the hazard that chromium poses to workers in the electroplating industry, stakeholders felt that decorative and hard chrome electroplating should be included as priority uses in this study. In addition, the categories of chromate conversion coatings and paints/pigments were mentioned as ones where there was the potential for worker exposure, and where the chromium still existed in the product in its hexavalent form. While there were concerns about chromium compounds in wood preservatives, it was felt that the use of CCA (chromated copper arsenate) was being phased out because of issues with its arsenic content, and that alternatives to CCA are already being implemented. Some other uses, such as in leather tanning or textile dying, were not listed as priorities because they no longer are important manufacturing uses in Massachusetts.

Priority Uses

Based on a review of stakeholder input, published research on environmental, health and safety issues, and the availability of alternatives, three general categories of use were selected as priorities for this study, with a fourth designated if time allowed (paints and pigments):

- Decorative chrome electroplating;
- Hard chrome electroplating;
- Chromate conversion coatings.

After discussion with industry representatives, the category of chromate conversion coatings was narrowed further to focus on only passivation of zinc and zinc alloy plated parts and zinc galvanized steel.

6.3 Alternatives Prioritization for Hexavalent Chromium

As described in the previous section, three hexavalent chromium use categories were selected for full alternatives analyses:

- Decorative Chrome Electroplating
- Hard/Functional Chrome Electroplating
- Passivation of Zinc Plated Parts and Zinc Galvanized Steel

The alternatives were prioritized using environmental health and safety, performance and the availability of information as the primary criteria. Cost may not be an important factor in evaluating hexavalent chromium alternatives since its severe toxicity is driving many manufacturers to adopt alternatives. For example, it is likely that the new PEL will be very difficult for many manufacturers to meet using traditional engineering controls such as local exhaust ventilation. In addition, EU directives are driving manufacturers to find hexavalent chromium-free alternatives.

6.3.1 Alternatives Associated with Decorative Chromium Electroplating

Available Alternatives

Within the category of decorative chrome electroplating, only two types of alternatives were identified:

- Trivalent chromium plating baths
- Low Temperature Arc Vapor Deposition (LTAVD) of trivalent chromium

Alternatives Screened Out

Both of these alternatives passed the initial environmental, health and safety screening criteria.

Alternatives Prioritization

Sufficient information regarding performance was available on each of the alternatives to proceed with a technical assessment. Therefore, both of the alternatives were selected for full assessments:

- Trivalent chromium plating baths
- Low Temperature Arc Vapor Deposition (LTAVD) of trivalent chromium

6.3.2 Alternatives Associated with Hard/Functional Chromium Electroplating

Available Alternatives

Many alternatives were identified for hard chrome electroplating:

- Electroless nickel and nickel composites
- Thermal sprays: high velocity oxy-fuel and plasma sprays
- Nickel-free electroplates and composites
- Weld facing methods and micro-arc welding
- Heat treatments and plasma nitriding
- Laser modification, alloying and coating
- Electrodeposited nanocrystalline cobalt-phosphorus coating
- Explosive bonding
- Physical vapor deposition/magnetron sputtering
- Chemical vapor deposition
- Nickel/Tungsten/Boron electroplating

Alternatives Screened Out

Based on the environmental, health and safety criteria, those alternatives that involved the use of nickel were screened out. Nickel is listed by IARC as a Group 1 chemical: sufficient evidence of carcinogenicity in humans. Consequently, electroless nickel and nickel composites, and nickel/tungsten/boron electroplating were not carried forward for technical assessments.

Alternatives Prioritization

In order to achieve a manageable list of alternatives for full assessment, two other alternatives were given a lower priority and dropped from further consideration. Nickel-free electroplates and composites had been mentioned only briefly in one reference. The research team was unable to find further information on this alternative, so it also was dropped. In addition, the explosive bonding alternative was determined to be a "niche" application, suitable only for a few very specific types of materials.

Therefore, the final list of alternatives to be assessed was as follows:

- Thermal sprays: high velocity oxy-fuel and plasma sprays
- Weld facing methods and micro-arc welding
- Heat treatments and plasma nitriding
- Nanocrystalline coatings
- Vapor deposition methods
- Functional trivalent chromium coatings

6.3.3 Alternatives Associated with Passivation of Zinc

Available Alternatives

Four alternatives were identified for passivation of zinc plated parts and zinc galvanized steel:

- Molybdates
- Trivalent Chromium Passivates
- Mineral Tie-Coat
- Combination Wet-Dry-Wet-Dry Process

Alternatives Screened Out

All of the alternatives passed the EH&S screening.

Alternatives Prioritization

Because very little published information was available on the combination wet-dry-wet-dry process, and the company that currently holds rights to the process did not respond to inquiries it was removed from the list of alternatives to be considered. Therefore, the following is the final list of alternatives for assessment for zinc passivation:

- Molybdates
- Trivalent Chromium Passivates
- Mineral Tie-Coat

6.4 Alternatives Assessment

6.4.1 Decorative Chromium Electroplating of Consumer and Automotive Products

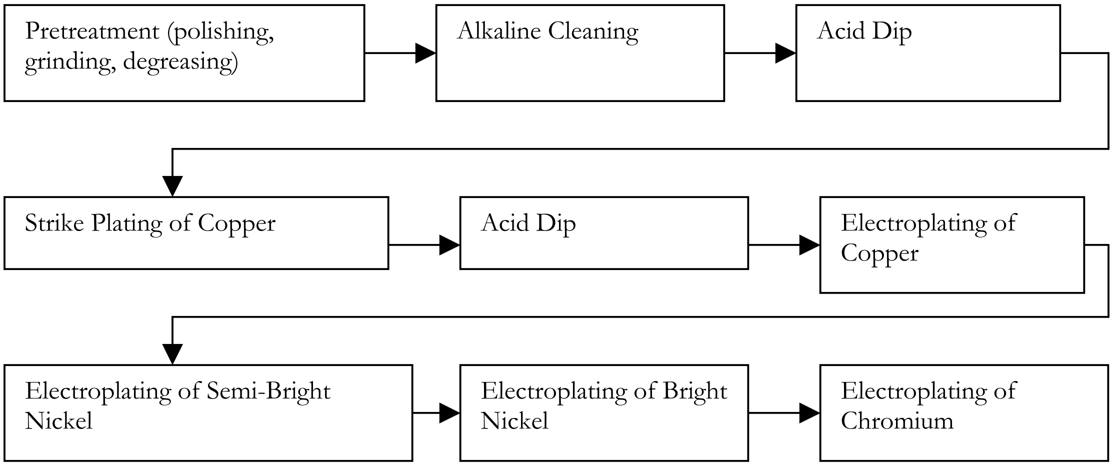
Existing Process

Decorative chrome plating (also known as bright chrome) is used for consumer applications such as appliances, metal furniture, plumbing fixtures, knobs and hand tools, and for automotive trim. It creates an attractive, blue-white finish, and helps to reduce tarnishing. Color, shininess and corrosion resistance are the key functional criteria for decorative chrome.

The decorative chrome layer typically is quite thin (0.002 to 0.02 mils) and is deposited onto a metal or plastic substrate over several layers of copper and/or nickel. The plating process has several steps, as shown in Figure 6.4.1 A.

Figure 6.4.1 A: Decorative Chrome Plating Process

(Oklahoma Department of Environmental Quality Air Quality Division 1999)

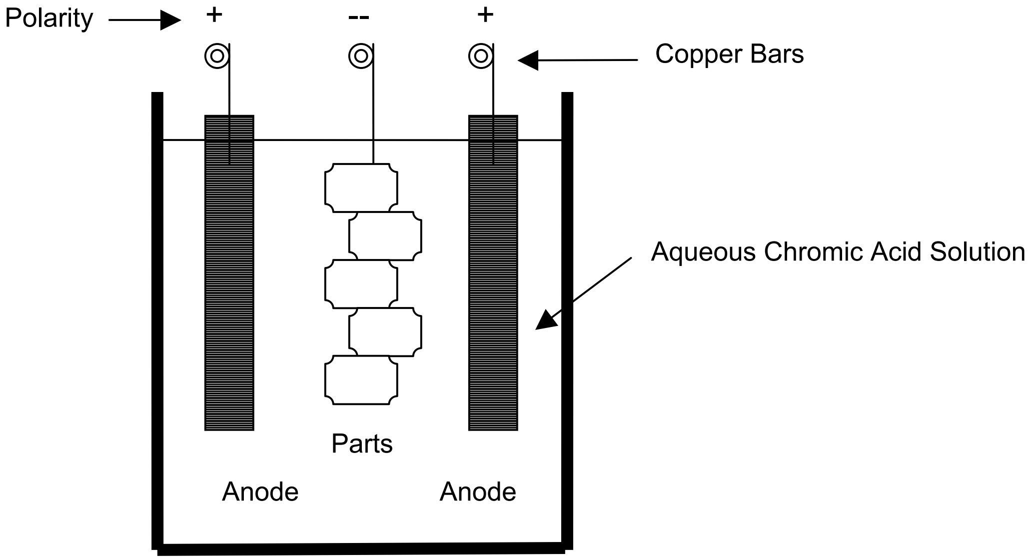


In the actual decorative chrome plating step, parts to be plated are hung from a rack in a tank that contains a hexavalent chromium electrolyte solution and anodes. Direct current is passed through the solution, which causes metal ions to be electrodeposited on the parts (cathodes). (Figure 6.4.1 B) The parts are baked after plating.

The major advantage of decorative hexavalent chromium is its appearance, especially its blue-white color. Functional disadvantages (in addition to health, safety and environmental problems) include poor throwing power/coverage, low resistance to burning during plating, the difficulty in removing impurities from the plating bath, problems in rinsing the plating solution from the plated parts (resulting in a large amount of "drag-out" hexavalent chromium), and intolerance to current interruptions/variations during plating (causing a discoloration known as "white wash") (Jones, Snyder 2005).

Two alternatives to decorative hexavalent chrome plating will be assessed for their feasibility: trivalent chrome plating and Low Temperature Arc Vapor Deposition (LTAVD®).

Figure 6.4.1 B: Hexavalent Chromium Electroplating



Technical Assessments

Trivalent Chromium Plating

The trivalent chromium plating process is basically the same as the hexavalent process, but with some operational variations. There are two types of trivalent chromium plating: single cell and double cell. Both of these processes prevent the formation of hexavalent chromium as a "side reaction" during plating. (California Department of Toxic Substances Control 1993) The single cell process includes an insoluble, inert graphite anode in the trivalent chromium solution with the parts to be plated. The double cell process has a lead anode that is separated from the solution by a membrane. Table 6.4.1A compares the single cell and double cell trivalent processes, and the hexavalent process.

Table 6.4.1 A: Chrome Plating Operating Conditions

(California Department of Toxic Substances Control 1993)

Operating Factor	Single Cell Trivalent	Double Cell Trivalent	Hexavalent Chromium
pH	2.3 – 3.5	3.3 – 3.9	< 1
Temperature, °F	70 – 120	70 – 130	110 - 115
Cathode Current density, A/ft^2	40 – 125	40 – 125	175 - 300
Agitation	Mild Air	Mild Air	Optional
Rectifier Voltage, V	4 – 15	4 – 15	4 - 12
Anode Material	Carbon	Lead – 7% zinc	Lead – 7% tin
Chromium Concentration, g/L	4 – 20	5 – 10	150 - 300
Max. Thickness at Room Temperature, mil	0.01 – 0.03	N/A	5 or more
Max. Thickness at High Temperature, mil	1 or more	About 0.01	N/A
Plating Rate at Room	0.005 – 0.007	N/A	0.005 – 0.007

Table 6.4.1 A: Chrome Plating Operating Conditions

(California Department of Toxic Substances Control 1993)

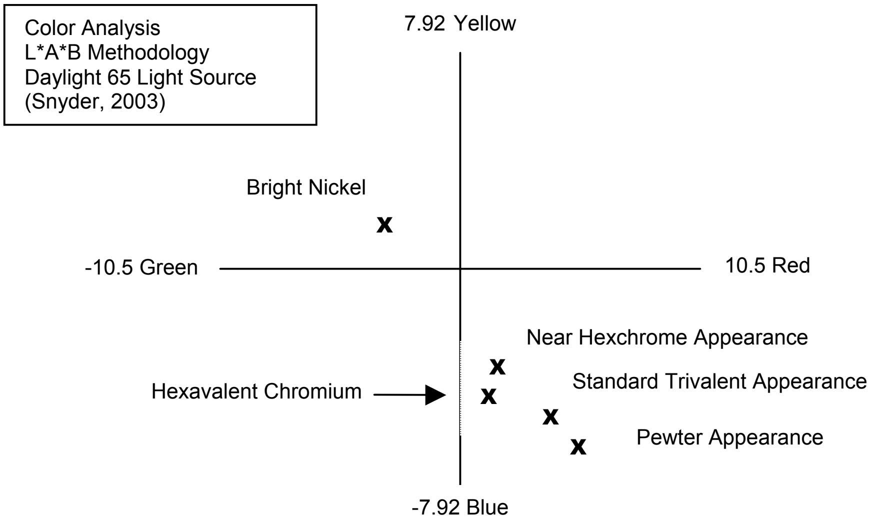
Operating Factor	Single Cell Trivalent	Double Cell Trivalent	Hexavalent Chromium
Temperature, mil/min			
Plating Rate at High Temperature, mil/min	0.007 – 0.010	0.004 or less	N/A

Although double-cell trivalent chromium electroplating was developed before the hexavalent process (both in the mid-19th century), the Cr(VI) process was simpler to use and therefore became the standard for decorative chrome plating. Commercially viable trivalent plating, using single-cell technology, became available in the 1970s. That technology generation had problems with color and plating rate that have since been overcome as the methodology has been refined and improved (Snyder 1988).

The darker, pewter-like appearance of parts plated with the earlier technology is attractive, but noticeably different from the blue-white hexavalent chromium finish. Use of a sulfate-based, double-cell process can produce trivalent plating that is very similar in appearance to hexavalent plating, if that parameter is important for the product consumer (Zaki 2002, 492-501). Varying the operating conditions during plating will produce deposits with different color traits, ranging from gray-black to "near hexavalent" (Snyder 2003). Figure 6.4.1 C compares the color of nickel, hexavalent and trivalent chromium plating; the intersection of the two axes represents "white standard appearance."

Figure 6.4.1 C: Color Analysis of Plating Types

(Snyder 2003)



While corrosion resistance for decorative chrome is less important than it is for hard chrome, it is appreciated by end users. A long-term atmospheric corrosion resistance test was begun in the 1970s at the LaQue Corrosion Center in North Carolina that compared a number of plating systems. ASTM Standard B456 for severe (SC3) and very severe (SC4) service conditions were used to compare test panels exposed to the elements over several years. Both hexavalent coatings made micro-porous and trivalent coatings (which are naturally micro-porous) performed well, exceeding the 10 years of corrosion resistance desired by automotive parts manufacturers. Trivalent plating outperformed untreated (not micro-porous) hexavalent plating (Snyder 2005).

Decorative trivalent chromium plating has many functional advantages over hexavalent chromium plating, as shown in Table 6.4.1 B:

Table 6.4.1 B: Advantages of Trivalent Chromium Over Hexavalent Chromium for Decorative Plating (Jones and Snyder 2005)

Factor	Trivalent Chromium	Hexavalent Chromium
Throwing Power	Good	Poor
Covering Power	Good	Poor
Tolerance to Current interruptions	Tolerant	Intolerant
Tolerance to Rectifier Ripple	Tolerant	Intolerant
Micro-discontinuous Structure	Micro-porous or micro-cracked	Special Process Required
Susceptibility to burning	Little	Great
Ease of Rinsing	Easy	Moderate
Color Buffing Required	Never	Occasional
Removal of Impurities	Easy	Hard
SO4, Cl, H3BO3 Contamination	No effect	Very Detrimental

Although the effect of impurities on the trivalent process is greater than for hexavalent chromium, the removal of impurities is much easier. Three methods of removing bath impurities are by dummy plating, chemical precipitation using a purifier, or continuous ion exchange (Zaki 2002).

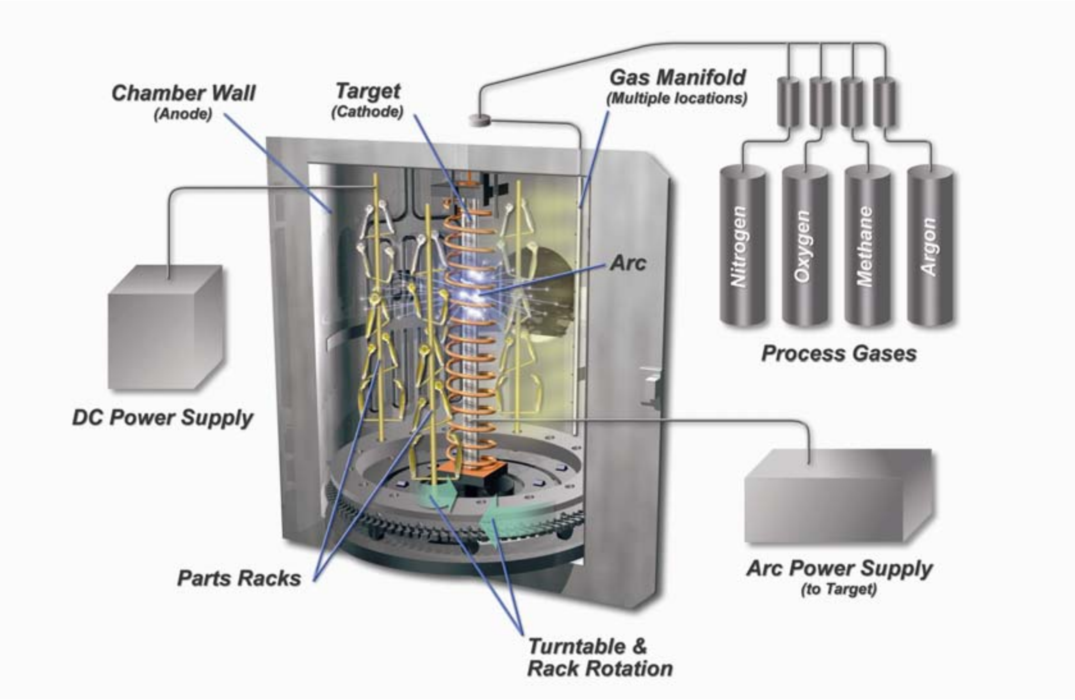
Low Temperature Arc Vapor Deposition (LTAVD®)

Low Temperature Arc Vapor Deposition (LTAVD®) is a proprietary form of physical vapor deposition (PVD See also Section 6.4.2.). It involves several steps:

- parts to be coated are placed on a turntable in a processing chamber under vacuum
- an inert gas (such as argon) is fed into the chamber
- a strong current is applied to create an arc across a solid metal target (cathode), evaporating the metal and sending off charged atoms
- the metal atoms and energized argon form a gas or plasma, which provides a conductive path that sustains the arc in the vacuum
- the parts are rotated around the target
- the gas containing the vaporized metal condenses on the parts, depositing a thin, solid film

By using different combinations of gases and metals, a variety of coatings with different characteristics can be formed. The specific combination of metals and gases chosen will dictate the color, hardness, and durability of the final coating (Sullivan, Larson 2005).

Figure 6.4.1 D: Low Temperature Arc Vapor Deposition (LTAVD®) Process
(Diagram reproduced courtesy of Vapor Technologies, Longmont, CO)



Most of the technical assessments of this proprietary process have been conducted by the company that holds the patent rights, Vapor Technologies of Longmont, Colorado. That company is a division of Masco Corporation, which is using the LTAVD technology for products produced by several of its companies, including Delta Faucet, Brass Craft, Weiser Lock, and Baldwin Hardware.

A major advantage of LTAVD is that it operates at room temperature, and the process does not heat the substrate. This means that a coating with a high melting point can be used on a substrate with a low melting point, such as plastic. Metals with dissimilar characteristics, such as titanium and aluminum, can be alloyed using the process, creating unique coating materials.

Parts are coated all over at one time (360 degree field), resulting in a very uniform coating. The rate of coating varies, with higher density and melting point metals having a slower rate. Adhesion to the substrate is good (Graves 1996).

In a 2005 article (Brondum, Larson 2005), Vapor Technologies reported on testing conducted on carbon steel coated with nickel base coats, and then with either a hexavalent chromium bath, or LTAVD-applied chrome or chromium nitride. CASS (copper accelerated salt spray) corrosion testing, spectrophotometer color testing, Vickers hardness testing and Taber abrasion testing were performed.

In 24-hour CASS testing, nearly all of the samples performed well. The main variable affecting performance was the type of nickel coating, rather than the chrome top layer. The LTAVD sample exhibited corrosion resistance that was similar or better than the hexavalent chrome samples.

With color being a key performance criterion for decorative chrome, the samples were compared using a spectrophotometer. The color difference (ΔE) between hexavalent and LTAVD chromium coated panels was measured at 1.4; differences less than 2.0 are generally not noticeable to the human eye.

In Vickers hardness testing, the LTAVD samples performed better than the hexavalent chromium samples. Cr(VI) coatings measured between 600 and 700 VHN; LTAVD chromium measured 800-1400 VHN, and PVD chromium nitride measured up to 2200 VNH.

Taber abrasion tests were done using a CS 10 wheel and a 1 kg load. The hexavalent and LTAVD chromium samples performed about the same on this test. LTAVD chromium nitride samples, however, were about 30% more wear resistant.

Financial Assessment

Trivalent Chromium Plating

Snyder (1988) prepared a comparison of the cost of waste treatment, which is a major considerations in plating, for typical trivalent and hexavalent plating processes. He estimated that the hexavalent treatment costs were nearly 10 times that of the trivalent process (Table 6.4.1 C).

Table 6.4.1 C: Estimated Annual Waste Treatment/Disposal Costs for Hexavalent and Trivalent Plating (Snyder 1988)

Operating Cost Factor	Hexavalent Chromium	Trivalent Chromium
Hexavalent Chromium Reduction	$1,480	---
Chromium Hydroxide Precipitation	$ 255	$ 38
Sludge Disposal	$3,805 (14,200 lb.)	$ 538 (2,000 lb.)
Total Annual Cost	$5,540	$ 576

Trivalent plating chemicals are more expensive than hexavalent plating chemicals, although that is likely to change as trivalent systems increase in popularity. The cost of chemicals, however, is offset by the greater efficiency of the trivalent process. In a case study conducted by the City of Los Angeles Department of Public Works in the 1990s, "net profit per shift" for a shop that converted to a trivalent process was about 15% higher than for the hexavalent process. Major reasons for the higher profit rate were the greater number of parts that could be put on each plating rack, and the higher rate of rejected parts with the hexavalent process. The Cr(III) plating also had lower waste treatment costs, required less auxiliary equipment such as tank ventilators, and less maintenance (Los Angeles Board of Public Works 1996) (Table 6.4.1 D).

Table 6.4.1 D: Comparison of Hexavalent and Trivalent System Costs

(Los Angeles Board of Public Works 1996)

Factor	Hexavalent			Trivalent		
	Unit Cost	**Qty Used Per Shift^**	**Cost Per Shift**	**Unit Cost**	**Qty Used Per Shift^**	**Cost Per Shift**
Plating Chemicals						
Chromic acid	$1.08/lb	28.8 lb	$31.10			
Chrome catalyst	15.00/lb	0.3 lb	4.32			
Trivalent additive #1				$28.75/gal	1.9 gal	$54.63
Trivalent additive #2				28.25/gal	1.5 gal	43.38
Trivalent base salts				1.97/lb	18.0 lbs	35.68
Boric acid				0.36/lb	10.0 lbs	3.60
Trivalent wetter				12.75/gal	0.6 gal	7.65
Hydrogen peroxide				8.00/gal	0.5 gal	4.00
Treatment Chemicals						
Sodium metabisulfite	0.33/lb	86.4 lbs	28.51			
Lime	0.09/lb	28.8 lbs	2.71			
Energy Usage						
Electrical	$0.085/kwh	196.0 kwh	16.66	$0.085/kwh	114.0 kwh	9.69
Natural Gas	$0.65/therm	6.9 thms	4.47	$0.675/therm	9.6 thms	6.24
Operating Variables						
Rejects		1.5%	81.00*		0.5%	27.00*
Operating Costs						
			168.77			190.87
Gross Profit Per Shift (Calculated at $0.20 per sq ft of parts plated)						
	0.20	7200 ft2**	1440.00	0.20	8220 ft2**	1644.00
Net Profit Per Shift (= Gross Profit - Oper. Costs)						
			$1271.23			$1453.13
Difference in Profits Per Shift (= Trivalent - Hexavalent)						
						$181.90

^ Shifts are eight hours in length.
* Cost for rerunning rejected parts.
** Trivalent Process is able to plate 15% more parts per shift, due to higher parts densities on racks.

Low Temperature Arc Vapor Deposition (LTAVD)

Cost information for this process has not been published; the process is being used by several major manufacturers of consumer hardware, indicating that it is commercially viable. Since a wide variety of gases and metals are used, material costs also would vary accordingly. A major operating cost would be energy. Waste treatment costs are likely to be minimal.

Environmental Assessment

Trivalent Chromium Plating

In hexavalent chromium plating, rinse water effluent must be treated with sulfur dioxide or sodium bisulfate to reduce the Cr(VI) to Cr(III). Zaki (2002) estimates that the volume of sludge generated by the hexavalent process is about 30 times that of the trivalent process.

Hexavalent plating typically involves the use of a lead-tin anode. While the double-cell trivalent process also uses this type of anode, the single cell process uses a less environmentally problematic graphite anode.

Trivalent plating involves the use of several chemical mixtures, which vary according to manufacturer. Using Enthone's Tricrolyte® (a single cell process) as an example, ingredients may include chromic sulfate, sodium sulfate, a proprietary ammonium compound, ammonium chloride, potassium chloride, ammonium formate, ammonium bromide, boric acid, butanedioic acid, sulfo-1,4-bis(1,3-dimethylbutyl) ester sodium salt, and ethanol. The manufacturer has not conducted "specific studies on the ecotoxicity or environmental fate" on the Tricrolyte® product.

Low Temperature Arc Vapor Deposition (LTAVD)

Vapor Technologies reports that the only effluent from this process is a small amount of vaporized oil from the vacuum pumps.

Human Exposure Assessment

Trivalent Chromium Plating

Trivalent plating involves the use of several chemical mixtures, which vary according to manufacturer. Using Enthone's Tricrolyte® as an example, ingredients may include chromic sulfate, sodium sulfate, a proprietary ammonium compound, a proprietary additive, ammonium chloride, potassium chloride, ammonium formate, ammonium bromide, boric acid, butanedioic acid, sulfo-1,4-bis(1,3-dimethylbutyl) ester sodium salt, and ethanol.

None of these chemicals is classified as carcinogenic, or is included on California's Proposition 65 list (chemicals known to cause cancer, birth defects or other reproductive harm). The MSDS notes that boric acid is a potential developmental toxin and ethanol is a proven developmental toxin. Many of the chemicals can be hazardous to human health if measures are not taken to avoid overexposure. Chemical specific effects from overexposure of the trivalent process chemicals are listed in Table 6.4.1 E.

Table 6.4.1 E: Potential Effects of Overexposure to Chemicals in Trivalent Plating Process Solutions (Source: Cookson Electronics MSDSs)

Chemical	Symptoms of Over-Exposure
Boric Acid	Skin, inhalation and ingestion: nausea/vomiting, diarrhea, drowsiness/fatigue, headache, low blood pressure. Lower body temperature, coma and possible death. Absorbed through the skin. Chronic weight loss, convulsive seizures, and skin rash or hives. Prolonged overexposure may cause damage to the teeth, liver and kidneys.
Ethanol	Eyes: blinking, redness or swelling. Skin: Defatting to the skin. Ingestion: dizziness/vertigo, euphoria, uncoordination, motor and sensory paralysis, developmental abnormalities. Inhalation: high concentrations of vapor may affect the central nervous system.
Chromic Sulfate	Eyes: may cause irritation or burns. Prolonged contact may cause eye damage. Skin: causes skin irritation. May cause sensitization by skin contact. Eczematoid dermatitis caused by trivalent chromium compounds has been reported. Inhalation: material is irritating to the mucous membranes and upper respiratory tract. Symptoms include coughing, shortness of breath/breathing difficulty, headache, fever, pulmonary edema. May cause sensitization by inhalation. Ingestion: can cause gastrointestinal disturbances. Symptoms include dizziness/vertigo, abdominal cramps/pain, nausea/vomiting, loss of consciousness/coma. Chromic effects: prolonged skin contact may cause dermatitis. Repeated of prolonged exposure to the substance can cause kidney damage. Inhalation may cause ulceration and perforation of the nasal septum.
Sodium Sulfate	Ingestion: fluid loss, blood in stool or urine, low blood pressure and high sodium levels.
Ammonium Chloride	Eyes and skin: irritating to the eyes, mucosa and skin and may cause burns. Causes dermatitis. Inhalation: material is irritating to mucous membranes and upper respiratory tract. Exposure can cause coughing, chest pains, difficulty in breathing. Ingestion: can cause gastrointestinal disturbances.
Potassium Chloride	Ingestion: drowsiness/fatigue, heart and circulatory problems. Large amounts can cause gastric upset and nausea/vomiting. Eyes: blinking, redness, or swelling. Skin: skin rash or hives.
Butanedioic acid, sulfo-,1,4-bis(1,3-dimethylbutyl) ester sodium salt	May be irritating to eyes, skin and respiratory system. Large amounts may cause gastrointestinal irritation, nausea, vomiting and diarrhea.
Ammonium Formate	Eyes: blinking, redness or swelling, pain. Skin: itching and pain. Inhalation: coughing, sore throat, breathing difficulty, shortness of breath and chest tightness/wheezing. Ingestion: gastrointestinal irritation.
Proprietary Ammonium Compound	Eyes: blinking, redness, swelling or pain. Skin: itching and pain. Inhalation: coughing, sore throat, breathing difficulty, shortness of breath and chest tightness/wheezing. Ingestion: gastrointestinal irritation.
Proprietary Additive	Eyes: tearing, blinking, redness or swelling. Skin: Defatting to the skin. May cause irritation. Inhalation: material is irritating to mucous membranes and upper respiratory tract. Ingestion: can cause gastrointestinal disturbances.

Recommended worker controls to prevent overexposure to the trivalent plating process chemicals include ventilation and eye, skin and respiratory protection.

Low Temperature Arc Vapor Deposition (LTAVD)

Information on possible human exposure factors for this process has not been published. The process is conducted in a sealed vacuum chamber, minimizing worker exposure to emissions. A variety of gases and metals can be used in the process; any hazards associated with those materials would be present. For example, a chromium nitride is deposited by feeding ionized chromium metal into a plasma of ionized argon and nitrogen. The chromium in CrN is trivalent. In addition, parts often are coated with one or more layers of nickel under the surface coating in order to improve corrosion resistance; this is true of hexavalent and trivalent chrome coated parts as well.

Table 6.4.1 F: Summary of Decorative Chromium Electroplating Alternatives

Assessment Criteria		**Cr(VI) (Reference)**	**Comparison Relative to Cr(VI)**	
			Trivalent Chromium	**LTAVD**
Technical/Performance Criteria	Corrosion Resistance	Good	=	=/+
	Appearance	Blue-white	-/=	=
	Throwing Power/Coverage	Poor	+	+
	Uniformity of Coating	Variable	+	+
	Tolerance to Current Interruptions	Poor	+	?
	Micro-discontinuous Structure	Need Special Process	+	?
	Susceptibility to Burning	High	+	**N/A**
	Ease of Rinsing	Moderate	+	**N/A**
	Color Buffing Required	Occasional	+	?
Financial Criteria	Effect of Impurities	Low	-	?
	Removal of Impurities	Difficult	+	**N/A**
	Waste Treatment & Disposal	Expensive	+	+
	Chemical Cost	Inexpensive	-	?
	Energy	196 kwh/8 hrs.	+	?
	Efficiency (number of parts per rack)	Moderate	+	**Varies**
	% Rejects	1.5%	+	?
Environ-mental Criteria	Amount of Waste Generated	High	+	+
	Use of Lead Anode	Yes	=/+	+

Table 6.4.1 F: Summary of Decorative Chromium Electroplating Alternatives

Assessment Criteria		Cr(VI) (Reference)	Comparison Relative to Cr(VI)	
			Trivalent Chromium	LTAVD
Human Health Criteria	Carcinogenicity	EPA Group A IARC Group 1	+	+
	Occupational Exposure: PEL (8-hour TWA)	˜ mg/m^3	+	+
	Skin Irritant/Sensitizer	Yes	+/=	+

Comparison Key + Better = Similar - Worse ? Unknown

6.4.2 Hard Chromium Electroplating of Industrial Components

Hard chrome plating, also known as functional or industrial chrome, typically is thicker than decorative chrome. It is used on industrial components that must perform under demanding conditions such as high temperatures, and repetitive grinding and impact forces. Unlike decorative chrome, appearance usually is not an important issue.

The two main reasons that hard chrome is used are to provide wear and corrosion resistance, and to rebuild worn components to precise dimensions. It has a low coefficient of friction, is hard and heat-resistant, adheres well to substrates of various geometries, and provides corrosion resistance. Industrial parts that often are hard chrome plated include aircraft engines and landing gear, oil well equipment, crank shafts, hydraulic cylinders, paper making equipment, molds, stamps, dies, drill bits, and power industry equipment.

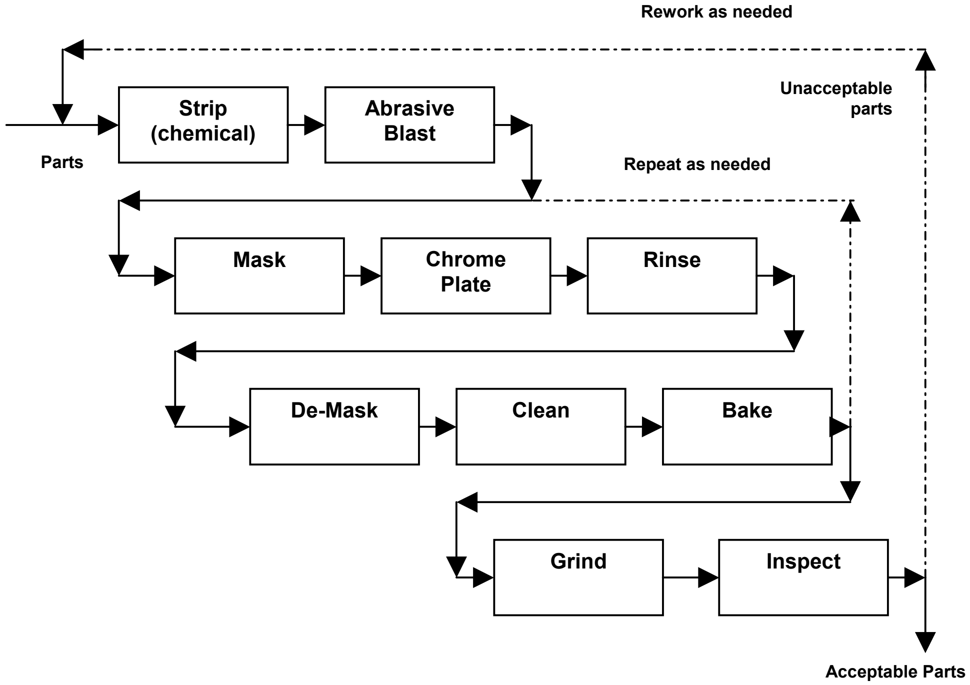
The key performance characteristics for replacements of the hard chromium include:

- Hardness
- Wear Resistance
- Embrittlement
- Fatigue Properties
- Corrosion Resistance
- Surface smoothness/machinability
- Application-specific performance such as hydraulic seal wear

The hard chrome plating process is a multi-step process that is essentially the same as that used for decorative chrome plating (Fig. 6.4.2A)(see Section 6.4.1). The coating thickness is greater, and parts may be plated more than once. Chromium is deposited from a highly concentrated solution of chromium oxide, typically 33 oz/gallon. In solution, the chromium exists in the hexavalent state and electrons for the electrodeposition reaction are provided by electrical current: $Cr^{+6} + 6e^{-} \Rightarrow Cr^{0}$. In addition to the chromium compound, hard chromium plating baths also contain catalysts for the deposition reaction. These typically are sulfate or fluoride/sulfate catalysts at low concentrations (~1% of the chromic acid concentration).

Figure 6.4.2.A: Hard Chrome Plating Process

(Sartwell et al. 2003)



Hard chrome plating has a number of limitations in addition to its health and environmental impacts. There are numerous steps in the plating process, and some steps may need to be repeated in order to get an adequate coating. The coating can be brittle, leading to failure or reduced corrosion resistance. In electroplating operations, plating thickness is generally greater on edges, corners and other high current density areas. This situation is greatly exacerbated in hard chromium electroplating. Intricately constructed anoding is required for even plating thickness.

Plating efficiency refers to the percentage of electrical current that is used directly for the deposition reaction. The major side reaction is splitting of water into oxygen (at the anode), and hydrogen (at the cathode). The efficiency of hard chromium plating baths ranges from 10 – 25%. Most other plating solutions range from 80 – 99% efficient. As a result of the low efficiency, a large quantity of gas is generated, which forms bubbles that rise to the top of the solution and break with enough force to generate significant chromic acid mist. The quantity of mist generated is also proportional to the viscosity of the solution, which is relatively high due to the high chemical concentration.

Maintenance of chromium plating tanks is essential to prevent solution contamination that adversely affects the quality of the plating. Solution contamination consists of:

- Excessive sulfate contamination. This is removed by the addition of Barium salts to create the insoluble barium sulfate.
- Trivalent chromium. Trivalent chromium is continuously formed during the oxidation-reduction plating reaction; it is also continuously reoxidized at the anode surface during plating. If the trivalent chromium concentration exceeds 1 – 2%, it is likely the anodes are scaled and require cleaning, or excess metallic contamination may be present. If the anodes are scaled, they may be descaled by plating with a high surface area "dummy" to reoxidize the trivalent chromium to the hexavalent state; chemically cleaning the anodes; or physically scrubbing the anodes.

Table 6.4.2 A: Functional Advantages and Disadvantages of Hard Chrome Electroplating

Advantages/Strengths	Disadvantages/Limitations
Deposit is extremely hard and wear resistant	Slow rate of deposition; multiple coats often needed
Thick deposits can be machined for repair/tolerance applications	Machining needed to get uniform thickness
Simple, well-understood technology	Susceptible to hydrogen embrittlement
Wide range of applications	Exhibits brittleness, leading to micro-cracking and reduced corrosion resistance
Surface offers good lubricity characteristics	Decontamination of plating solutions is difficult
In combination with nickel underplating, it can offer good corrosion resistance	

- Metallic contamination. This can cause plating quality problems such as rough deposits, hazy or milky deposits, or a decreased bright range. Membrane electrolysis or the use of "Porous Pot" technologies can remove excess metallic contamination, as well as re-oxidize trivalent chromium to the hexavalent state. Extensive contamination of the solution may require replacement of some or all of the solution.

During the plating process, the base material may absorb hydrogen generated during the plating operation, resulting in hydrogen embrittlement. Hydrogen embrittlement is the phenomenon by which absorbed hydrogen migrates to grain boundaries in the base material, seriously weakening the part. If not post-treated by a bake cycle (typically 375° F for 24 hours, but varies depending on base material), cracking of the base material may occur, causing failure of the part.

Hard chromium plating may need to be stripped from the part for repair purposes or due to quality defects. In either case, stripping is accomplished using a strong sodium hydroxide solution and electrical current. This creates a corrosive, toxic hazardous waste that must be disposed of.

Description of Alternatives

Six categories of alternatives to hard chrome plating were selected for study:

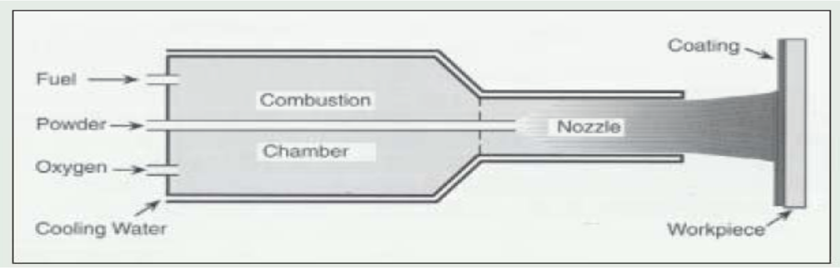
- Thermal sprays
- Weld facing methods
- Heat treatment methods
- Vapor deposition methods
- Nanocrystalline coatings
- Functional trivalent plating

It should be noted that some of these categories include several related processes that differ in their functional details, and a variety of metals can be deposited with most of the processes. In addition, the categories often overlap to a certain extent, with a particular process sometimes being classified differently by various scientists.

Thermal Sprays

Thermal spray is a coating process in which wire or metallic powder is melted by a high temperature flame and sprayed as particles or droplets onto a substrate. During the application the spray torch used makes several passes as it accelerates the soft powder into the surface.

Figure 6.4.2 B: HVOF Process
(Devereaux, Stricklin 2004)



A type of thermal spray that is being used as a hard chrome replacement is high velocity oxy-fuel (HVOF). HVOF involves metal powders (e.g. cobalt, tungsten) being heated in a combustion chamber by an oxygen/fuel gas mixture and expelled at high velocity and temperature (up to 1,800 m/s and 2,700° C) onto the material to be coated (Hermanek 2001).

Weld Facing Methods

Weld facing (also know as hard facing) is a dry method of joining a hard coating, edge, or point to a metal or alloy substrate to improve its resistance to abrasion, corrosion, heat or impact. It also is used to restore worn surfaces.

The weld facing process involves applying metal or ceramic to a part with welding equipment. That equipment can be the traditional oxyacetylene welding torch, one of the many types of arc welders, or a type of specialized micro-arc welder. Micro-arc welding uses very small energy levels and is good for use on conductive surfaces; this category includes Electro Spark Deposition (ESD), which is used in the open air with a hand held electrode for repairs over small areas, and Electro Spark Alloying (ESA), a technique used over a much smaller area. Also included in this category is laser cladding -- the melting of metallic powder on to the surface of a substrate using the finely controlled energy of a laser beam.

Laser alloying is a surface modification technique where a ceramic/metal (cermet) coating mixture is heated using a laser to fuse the coating to the substrate. It forms a thin, permanent alloy layer. A variant on laser alloying is laser induced surface improvement (LISI^{TM}), which was developed at the University of Tennessee Space Institute. These processes are intended to make a surface more resistant to corrosion and wear, and to increase hardness.

Laser alloying is similar to laser cladding. One way to differentiate one technique from the other is by comparing the relative amounts of the consumable material added and the substrate melted. The two categories are arbitrarily separated by their relative amount of dilution, with laser alloying having a greater percentage of dilution than laser cladding. (www.lvitech.com/technology_cladding_2.htm)

Heat Treatment Methods

These methods, sometimes called thermal diffusion methods, use heat to diffuse elements into the top surface of a substrate metal to form an alloy or layer with desired properties, such as hardness or lubricity. The names of some of the processes in this category are derived from the type of element used: nitriding (nitrogen), boronizing (boron), and carburizing (carbon.)

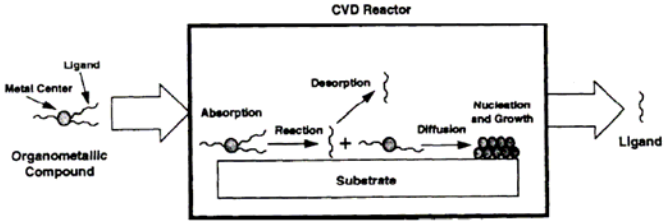
Plasma diffusion is the process whereby elements are introduced into the surface of the substrate by the use of a gas activated with the desired element at elevated temperatures. Variations on this process include plasma nitriding, nitrocarburizing, and low pressure nitiriding. (plasmaindia.com)

Vapor Deposition Methods

Physical vapor deposition (PVD) employs a coating material created from a solid that is vaporized by an electric arc or an electron beam. The material is then transported through a vacuum, low-pressure gas or plasma (which accelerates the ions), condensing on the component surface and forming a thin and very hard layer. Types of PVD processes are ion plating, vacuum evaporation, thermal evaporation, electron beam evaporation, and sputter deposition (Mattox 2001; Singh, et al. n.d.)

Chemical vapor deposition (CVD) is similar to PVD; however, the coating material comes from the gases that combine on the hot surface to form the hard coating. Variations on the CVD process include atmospheric CVD (conducted at atmospheric pressure and high temperature); low pressure CVD (sub-atmospheric pressure and high temperature); and plasma enhanced CVD (lower temperature with heat generated by an electrical plasma.) (National Defense Center for Environmental Excellence (NDCEE) 1995)

Figure 6.4.2 C: Chemical Vapor Deposition (NDCEE 1995)



Nanocrystalline Coatings

This process involves deposition of very small grains (5-15 nm) of crystalline alloys (for example, cobalt-iron-phosphorus) on a metal substrate (McCrea, Marcoccia & Limoges 2003). Nanocrystalline materials exhibit unique properties resulting from the large proportion of grain boundary atoms (Tjong, Chen 2004). Hardness, fracture toughness and yield strength increase as the size of article grains get smaller; this is known as the Hall-Petch effect (Klingenberg, Broonam & Naguy 2005). The coating can be applied through electrodeposition, vapor deposition, or spray conversion processing.

Trivalent Chromium Plating

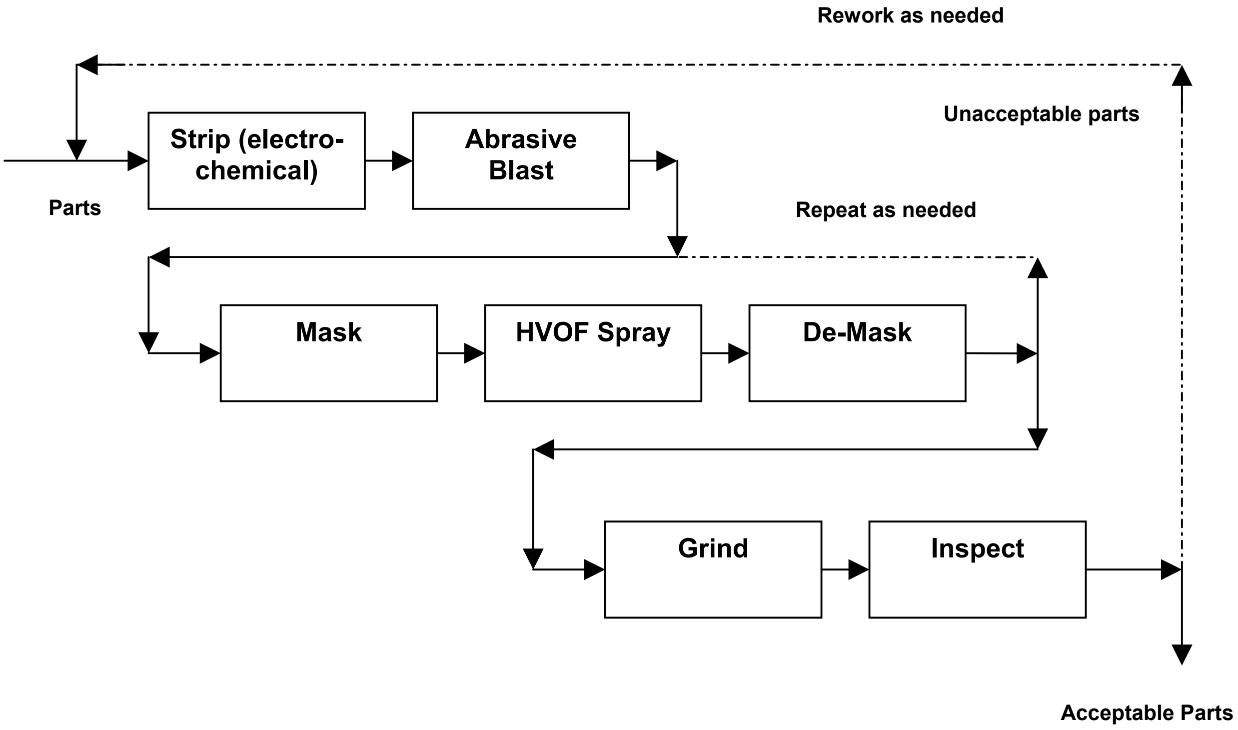
Conventional trivalent chromium plating is not suitable for replacing functional (hard) chrome because its low plating efficiency and low plating rate limit the thickness of trivalent deposits to no more than 0.1 mil/2.5 μm. (Renz et al. 2003) The United States Environmental Protection Agency's Small Business Innovation Research Program funded development of a trivalent chromium alternative to hard chrome plating that attempts to overcome that limitation. Faraday Technologies' Faradaic™ process is similar to the wet hexavalent plating process, with the capability to plate a thick, functional chromium coating using a trivalent chromium plating bath. Described as a charge modulated electrochemical deposition (CM-ECD) process, it is intended as a "drop-in" alternative to hexavalent baths.

Technical Assessment

Thermal Sprays

High velocity oxy-fuel (HVOF) is a type of thermal spray/dry spraying process that is capable of depositing a wide array of single-metal, alloy, cermet and ceramic coatings that can provide similar or better functional characteristics than hard chromium plating. Figure 6.4.2 D shows the steps in the HVOF process.

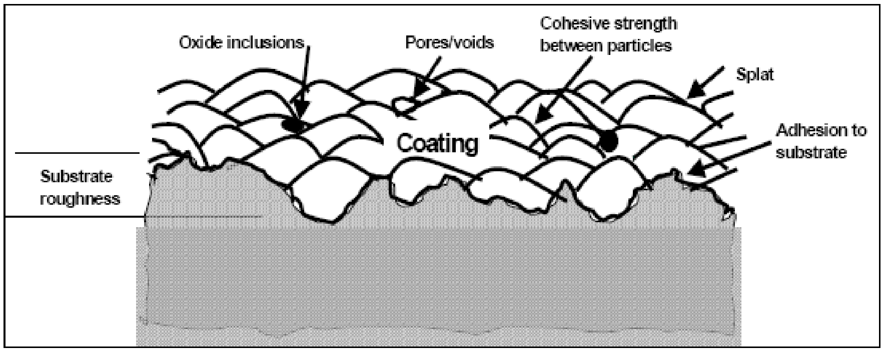
Figure 6.4.2 D: HVOF Process
(Sartwell et al. 2003)



The HVOF spray process uses pure oxygen mixed with one of a variety of fuels such as propane, acetylene, hydrogen, etc. to generate supersonic gas velocities on the order of 1,800 m/s. The material to be deposited is in the powder form, generally 20 – 100 µm in size (Sartwell, et al. 1999). The powder is fed into the spray gun combustion chamber, along with the oxygen and fuel, and the combustion heated stream, at approximately 2,700° C is directed at the part to be coated. Typical distances from the spray gun to the part are 15 – 30 cm (Sartwell, et al. 1999).

As the materials are heated, the particles change to a more plastic (or molten) form. The coating is formed as the particles impinge on the surface, flatten and form platelets (splats) that build a laminar, non-homogeneous coating (United States Army Corps of Engineers 1999). The degree of porosity in the coating is dependent on the materials and processing conditions. The deposition rate is approximately 0.002 in. per minute (Sartwell, et al. 1999). The total time to coat a part will depend on part configuration and size as well as the speed of the spray gun and/or part relative to each other. Thicknesses in excess of 0.1 in. may be deposited (Fedrizzi, et al. 2004).

Figure 6.4.2 E: Cross Section of a Typical Thermal Spray Coating
(United States Army Corps of Engineers 1999)



One drawback to HVOF is that it cannot be used to deposit materials on internal diameters – it is a "line of sight" deposition process. There are other thermal spray technologies such as plasma spray that are being developed to allow internal diameter coating (Legg, Sauer 2005). Additionally, due to the high temperatures involved, heat sensitive components may be damaged.

Examples of coating materials[9] that can be applied by HVOF include (Stokes 2003):

- Tungsten carbide/cobalt (WC/Co) – various percentages of WC and Co
- Aluminum bronze alloy
- Copper
- Cobalt base superalloy
- Aluminum alloy/polyester

Some applications for the HVOF coatings include (Stokes 2003):

General Manufacturing Industry:	Extrusion Dies, Thread Guides, Forging Tools, Wire Drawing Capstans, Cam Followers, Roller Bearings, Hot Forming Dies
Gas Turbine Industry:	Turbine Nozzles, Jet Engine Ducts, Jet Engine Manifold Rings, Gas Turbine Fan Seals, Aircraft Flap Tracks, Expansion Joints, Mid Span Supports (Fan Blades)
Petroleum Industry:	Pump Plungers, Liners, Sleeves, Compressor Rods
Chemical Process Industry:	Gate Valves, Pump Components
Paper/Pulp Industry:	Printing Rolls, Digesters, Liquor Tanks
Automotive Industry:	Piston Rings, Cylinder Liners

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[9] There are also several nickel-based coatings that are used: Nickel/Chromium/Molybdenum, Nickel/Chromium/Iron, Fusible Nickel Based Alloy, Nickel Based Alloy/Tungsten Carbide, and Chromium Carbide/Nickel Chromium.

HVOF coating materials are chosen on the basis of function, such as improvements in fretting wear, abrasive wear, corrosion control, high or low temperature application, etc.

The Hard Chrome Alternatives Team (HCAT) is a bi-national team comprising a U.S. team concentrating on replacing chrome plating in Department of Defense (DoD) repair depots, and a Canadian team working primarily to replace chrome on commercial and military aircraft landing gear. They have performed extensive testing and data collection/analysis on HVOF. Their work can be accessed at: http://www.hcat.org/) Much of the literature on HVOF has been produced by HCAT.

There are many materials/material combinations that can be deposited by HVOF. For the replacement of hard chromium plating on aerospace components, the primary material that has been extensively tested is WC-Co (Tungsten carbide/cobalt), a cermet (ceramic/metallic) material.

The choice of materials must be carefully considered. In some cases, coatings optimized for wear resistance have exhibited poor base-material fatigue properties (Legg, Sauer 2000). Optimization of the coating materials must consider both the base material and coating properties and interactions.

Hardness

Typical requirements for hard chrome hardness are 850 – 1000 Vickers (VHN). In one study conducted on gas turbine engine components, HVOF deposited WC-Co was found to have hardness values >1,100 VHN. In research conducted by the Naval Research Laboratory, WC-Co coatings were found to have average Vickers hardness of 1,220 versus an average hard chrome hardness of 873 VHN (Sartwell, et al. 2003).

Wear Resistance

"ASTM G65 Standard Test Method for Measuring Abrasion Using the Dry Sand/Rubber Wheel Apparatus" is the method that covers laboratory procedures for determining the resistance of metallic materials to scratching abrasion by means of the dry sand/rubber wheel test. In tests performed by Sulzer Metco, hard chromium had a mass loss of 60.6 mg, while various WC-Co alloys applied by HVOF had no greater than 40.6 mg (Kirsten, et al. 2005). Another ASTM G65 test performed by Hart et al. showed a volume loss of ~28 mm^3 for an HVOF applied WC-metal alloy versus ~52 mm^3 for hard chrome (Hart et al.)

Fatigue Properties

Substrate fatigue occurs during hard chromium plating as the stress in the deposit increases, increasing the residual stress at the substrate surface. This can lead to reductions in the fatigue strength of the substrate, resulting in fracture of the part (Nascimento, et al. 2001). HVOF offers significantly improved fatigue properties.

Embrittlement

Because hydrogen is not generated during HVOF processing, as it is in hard chrome plating, embrittlement of the substrate material is not a concern.

Environmental embrittlement stress corrosion cracking occurs as a result of exposure to materials in the environment (such as salt). Susceptibility to this phenomenon is tested via Test Method F-519 notch test (Sartwell et al. 2003), and has been performed by the Hard Chrome Alternatives Team. Their data show that HVOF performs much better than hard chrome, that is, the parts are less susceptible to this type of embrittlement.

Corrosion Resistance

Hard chromium plating is a barrier coating in regards to corrosion resistance. If the barrier is breached, corrosion of the substrate material will occur. HVOF coatings also act as a barrier coating, but in this case, the coating itself will corrode, typically due to dissolution of the cobalt in the coating (Legg, Sartwell). This may result in some flaking of the coating, but not the catastrophic failure that can occur with hard chrome when the underlying surface corrodes, delaminating the coating from the substrate.

The primary effect of HVOF corrosion is roughening of the surface, which can reduce the life of seals associated with hydraulic units. However, testing so far has shown that under service-life conditions, corrosion is not evident (Legg 2000).

Surface smoothness/machinability

Hard chrome plating is often used for repair of equipment. The worn area is plated to a thickness greater than required, then ground and/or polished to the specified dimension. For hydraulic seal applications, as well as other critical sliding applications, a smooth finish is critical to prevent seal wear and subsequent hydraulic fluid leakage. The HVOF finish is similarly capable of being ground and polished to fine or superfine finishes (Nuse, Falkowski 2000).

Application-specific developments

HVOF-applied coatings have been approved for landing gear components on the military A-10, C-130, C-141, and other aircraft, as well as certain F-22 engine components. Boeing and Airbus also have specified HVOF coating on various commercial aircraft equipment parts (Sartwell et al. 2003).

Table 6.4.2 B: Advantages and Limitations of HVOF as a Hard Chromium Electroplating Alternative (Sartwell et al. 2003)

Advantages/Strengths	Disadvantages/Limitations
Higher hardness, better wear resistance, longer overhaul cycle, less frequent replacement	Brittle, low strain-to-failure; can spall at high load (issue primarily for carrier-based aircraft)
Better fatigue, corrosion, embrittlement	Line of sight only. Cannot coat internal diameters
Material can be adjusted to match service requirements	More complex than electroplating. Requires careful quality control.
Can coat large areas quickly. Can be chemically stripped. Many commercial vendors.	WC/Co requires diamond grinding wheel. Only HVOF can be plunge ground.
No air emissions, no high volume rinse water.	Co toxicity

Weld Facing Methods

Weld facing methods generally are used for the rebuilding of worn parts, one of the primary uses of hard chrome. The forms of weld facing most likely to be used in replacing hard chrome are electrospark deposition (ESD) and laser alloying.

The team that is investigating alternatives to hard chrome for military applications (Hard Chrome Alternatives Team – HCAT) categorizes ESD as being appropriate for "niche" applications, such as on-site repair of small areas of localized damage to metal parts, where the material to be deposited is the same as the parent material. It has been used for repair of gas turbine engine (GTE) parts, and for shafts of ships, submarines and vehicles. Table 6.4.2 C lists some of the advantages and disadvantages of ESD for repair of worn parts:

Table 6.4.2 C: Advantages and Disadvantages of ESD for Repair of Worn Parts

Advantages	Disadvantages
Inexpensive, portable, can repair-in-place	Very slow
Can get into very small spaces and re-entrant geometries	Some materials (carbides) self-limiting in thickness
Wide variety of coating materials	Coating has high tensile stress; cracks common, fatigue debit
Hand-held or robotic	Rough surface; sometimes have to file between layers
Very thin heat-affected zone (HAZ)	

The National Defense Center for Environmental Excellence (NDCEE 2003) has evaluated the feasibility of using ESD to replace hard chrome in applications where some of the other hard chrome alternative, such as HVOF, are not suitable. It found that ESD rebuilt surfaces with a hardness and smoothness that were comparable to hard chrome, and that wear performance was similar or better.

Another weld facing method is Laser Induced Surface Improvement (LISI). Developed by the University of Tennessee Space Institute (UTSI), it has been tested at the United States Air Force's Arnold Engineering Development Center (AEDC). The results of the testing have not been published, but UTSI indicates that it can be effective in improving corrosion resistance, wear resistance, and hardness. Although there have been some trials using the technique for applications such as tractor-trailer fifth-wheel hitches, no company has adopted it on a commercial level, and the project team has disbanded (Dahotre, pers. comm. 2006).

Heat Treatments and Plasma Diffusion

Unlike weld facing methods, heat treatments are not suitable for rebuilding parts. Rather, they are used to make surfaces more resistant to wear, corrosion or oxidation (Rowan Technologies, n.d.) They have the advantage of being commercially available, well-defined processes, and can be used for large parts (such as hydraulic rods and pistons) (Legg 1999). A key disadvantage is that the part is subjected to high temperatures (500-1000° C), which can distort or melt some alloys.

Plasma nitriding (sometimes called ion nitriding) does not involve the very high temperature of traditional heat treatments. The plasma typically is 400-590°C, making it an option for a greater range of metals. As a replacement for hard chrome, it may be used in combination with another process. For example, a substrate is hardened with plasma nitriding, and then coated with a Physical Vapor Deposition (PVD) process.

Northeast Coating Technologies, a company that performs plasma nitriding, lists the following advantages of the process over hard chrome:

- It imparts a hard, wear resistant diffused layer, without problems with flaking, spalling, edge build-up, and chipping
- Cutting edges remain sharp during plasma nitriding, and the process achieves a consistent hardness and case depth
- There is no build-up that causes the rounding of edges and webbing at the base of cavities
- Ion nitriding provides good resistance to indentation
- It improves the fatigue strength of the material

A German company (Metaplas Ionon) tested their patented IONIT OX process, which is suitable for ferrous materials, in comparison to hard chrome. The results are shown in Table 6.4.2 D.

Table 6.4.2 D: Characteristics of Corrosion-Protection Processes for Steel, IONIT OX Compared to Hard Chromium Electroplaing (auf dem Brinke and Krug, 2001)

Factor	Chromium Electroplating	IONIT OX
Treating Temperature, °C	<100	500-580
Environmental Concern	Cr(VI)	CO_2/NOx
Coating	Chrome with Cr(VI)	Oxide
Structure	Porous, brittle	Dense
Depth, mm	20	0.2-0.3
Vickers Hardness, VHN	900	800-1400
Hardness Gradient	Steep	Very good
Salt Spray Test Duration, h	300	500
Production Costs	High	Low

Nanocrystalline Coatings

Much of the research on this method has been conducted by a team that originally worked in the Canadian power industry (Integran Technologies). The United States Department of Defense Strategic Environmental Research and Development Program (SERDP) sponsored development and refinement of the method, with a goal of replacing hard chrome at Department of Defense rework, maintenance and manufacturing facilities (SERDP, n.d.). Additional work on using nanocrystalline coatings for non-line-of-sight applications has been done under the auspices of the Air Force Research Laboratory, and the Department of Defense's Hard Chrome Alternatives team (HCAT). A Massachusetts company, Xtalic, Inc., also has developed nanotechnology that can be used to replace hard chrome.

The interagency Strategic Environmental Research and Development Program (SERDP), a joint venture of the United States Department of Defense, Department of Energy, and Environmental Protection Agency, sponsored a three year, three-phase study of nanocrystalline coatings as a replacement for hard chrome on non-line-of-sight applications. In the first phase evaluation was done on three alloy coatings – cobalt-phosphorus (Co-P), cobalt-molybdenum (Co-Mo) and cobalt-iron-phosphorus (Co-Fe-P). The second phase looked at performance characteristics of a electrodeposition process using the Co-P alloy. The third phase involved applying the Co-P coating on test internal-diameter (ID) pieces, and to an actual landing gear shock strut. Tables 6.4.2 E and 6.4.2 F summarize some of the test results from that project (McCrea, Marcoccia & Limoges 2003).

Table 6.4.2 E: Nanocrystalline Co-P Process Data Summary Compared to Hard Chromium Electroplating (McCrea et al. 2003)

Factor	Nano Co-P Alloy	Hard Chrome
Bath Chemistry	Co 2-twt%P ($CoCl_2$/H_3PO_4/H_3PO_3)	Cr (CrO_3/So_4^{-2})
Efficiency	85-95%	15-35%
Deposition Rate	Up to 8 mil/hr	Up to 1.6 mil/hr
Thickness	Demonstrated up to 0.020"	Typically <0.005"
As-deposited Appearance	Pit/Pore Free	Microcracked
Microstructure	Nanocrystalline	----
Relative Process Cost	1.3	1.0
Emission Analysis	Below OSHA limits	Cr^{+6}

Table 6.4.2 F: Nanocrystalline Co-P Property Data Summary Compared to Hard Chromium Electroplating (McCrea et al. 2003)

Factor	Nanocrystalline Co-P	Hard Chrome
Hardness (as deposited)	600-700 VHN	800-1200 VHN
Hardness (heat treated @ 250° C)	700-800 VHN	----
Hardness (heat treated @ 400°C	1000-1200 VHN	----
Ductility	2-7% elongation	<0.1%
Thermal Stability	400° C	----
Wear (Abrasive – Taber)	27 mg/1000 cycles (CS-17)	3.2 mg/1000 cycles (CS-17)
Wear (Adhesive – Pin on disk)	11 mg/1000 cycles (CS-10)	1.0 mg/1000 cycles (CS-10)
Corrosion (Salt Spray)	Protection Rating 8 @ 1000 hours	Protection Rating 2 @ 1000 hours
Corrosion (Potentiodynamic)	0.1-1 mpy	0.01 mpy
Internal Stress	10-15 ksi (tensile)	Cracked – exceeds cohesive strength
Hydrogen embrittlement	None	Yes – min. bake 24 hrs.
Fatigue	Retesting required	Fatigue debit

The nanocrystalline Co-P coating compared favorably with the hard chromium electroplating in most respects:

- Efficiency of the coating process was greater
- Deposition rate was greater
- Air emissions were below OSHA limits
- Ductility was greater
- Sliding wear resistance was greater
- Corrosion resistance was greater (with the exception of Co-Fe-P alloys)
- Tensile strength was greater
- Hydrogen embrittlement did not occur

The functional areas where only some of the nanocrystalline coatings equaled hard chrome were abrasive wear and hardness (which usually are correlated.)

The hardness of the nanocrystalline deposits varied according to the amount of phosphorus used and whether a heat treatment was added at the end of the process. Samples were subjected to a Vickers hardness test, which measures the hardness of metals. A pure nanocrystalline cobalt exhibited a Vickers Hardness Number (VHN) of 550; this increased to a VHN of over 800 with a Co-P alloy with 5 percent (weight) phosphorus. The addition of a short (ten minutes) annealing time at 400 degrees C further increased the hardness to 1000 VHN or more. This is close to the maximum VHN for hard chrome.

Abrasive (Taber) Wear testing of the nanocrystalline coatings generally showed them to be less resistant to wear than hard chrome. The Taber Wear Index (TWI) is measured in mg per 1000 cycles; a lower index number means that the material is more wear resistant. Hard chrome has a TWI of 3.4. The pure cobalt samples had TWIs of more than 38. The Co-P coatings had TWIs between 12 and 30 (depending on the amount of phosphorus, and annealing time/temperature.) A Co-High Fe-P alloy showed a TWI of 11.0, and a Fe-Low Co-P sample had a TWI of 6.8. The only sample that was comparable or better than hard chrome in wear resistance was a Co-P alloy with added boron carbide (B_4C): its TWI was 2.3. Some of the test results indicated that the texture of the crystals had an effect on their wear resistance.

The Air Force/HCAT team compared hard chrome plated steel panels with several nanocrystalline coated panels. A variety of electroplated and electroless coating formulas were tested, some of which featured occluded diamond particles.[10] Federal specification QQ-C-320B for electrodeposited chromium engineering plating (Class II) was used as a guide for evaluation (Klingenberg, et al. 2005).

A minimum coating thickness of 2 mils (0.002 in.) – the thickness that the specification dictates for hard chrome -- was required in order for samples to be considered adequate. Only the electrodeposited Nano-Co with 2000 nm WC met this standard, but several others came close to it. The project team felt that fine-tuning the plating process was likely to improve the performance of the electroless nano-coatings in respect to this parameter.

All samples except the electroless Co-B passed the adhesion test (ASTM B571). There were some questions as to whether the re-use of the test panels (they had been coated, stripped and re-coated) affected the adhesion of the Co-B coating.

In the test for hardness, most of the nano coating did not achieve a hardness level comparable to hard chrome. The exceptions were the Co-P and Co-P/diamond coatings, which met or exceeded the hard chrome standard. This result is similar to that of the SERDP study; the inclusion of phosphorus in the coating makes it harder.

The nano-coatings that did not have occluded diamond particles failed the Taber wear resistance tests. Those that did have the diamond particles, however, performed better than the hard chrome sample.

Vapor Deposition Methods

Physical Vapor Deposition (PVD) is a method of building a thin film, atom by atom, on the surface of a substrate. The solid or liquid coating material is placed in a vacuum or low pressure plasma environment where it vaporizes and condenses back into the solid phase on the surface of the substrate. There are many variations of this process, some in a vacuum environment, with or without ion beam assist, and some in a low pressure plasma environment. Each is unique in the way that the coating material is generated and deposited, but all share the common vapor deposition process. A few of the PVD variations are described below.

Vacuum evaporation is the most basic of these processes. The source (coating) material is thermally vaporized in a vacuum, and follows a “line of sight” trajectory to the substrate where it condenses out as a solid film. Vacuum evaporation is widely used in diverse industries, for applications such as mirror coatings, barrier films on flexible packaging, as well as corrosion and wear resistant coatings.

The more advanced methods of vacuum evaporation use “ion assisted deposition” or ion plating to enhance the quality of the deposited film. Ion plating bombards the depositing film with energetic particles. The energetic particles may be the same material as the depositing film, or it may be a different inert (argon) or reactive (nitrogen) gas. In a vacuum environment where the ions originate from an ion gun, the process is termed “ion beam assisted deposition” (IBAD) (Mattox 1999). The US Department of Defense has done a considerable amount of development of these types of coatings for aerospace and defense applications.

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[10] Several nickel-alloy coatings also were tested; some of these performed better than the non-nickel alloys.

Sputtering is a non-thermal vaporization process where the surface atoms on the source material are physically ejected from the solid surface by the transfer of momentum from bombarding particles. Typically the particle is a gaseous ion accelerated from a low pressure plasma or an ion gun (Mattox 2001). Sputtering is widely used in the semiconductor and other industries for thin film metallization.

These processes can be used to apply many elements, alloys or compounds to the surface of a substrate. PVD coatings that are potential substitutes for hard chrome plating include:

- titanium nitride (TiN)
- titanium-aluminum nitride (TiAlN)
- zirconium nitride (ZrN)
- chromium nitride (CrN)
- chromium carbide (CrC)
- diamond-like carbon (DLC)
- silicon carbide (SiC)

In addition, multi-layer deposits (e.g., TiN / Ti / TiN) can provide improved corrosion resistance with a thinner overall coating (Navinsek, et al. 1999).

The quality of the substrate surface also directly effects the quality of the deposit and its corrosion resistance. An irregular surface, or one with many defects or contaminants will not produce a good, corrosion resistant finish. Similarly, the surface preparation and resulting cleanliness of the substrate surface also heavily influence the final finish quality.

Legg (1999) notes that PVD coatings are being tested by the Department of Defense for the inside of gun barrels. Table 6.4.2 G lists some of the advantages and disadvantages of the PVD process for replacing hard chrome on internal diameters.

Table 6.4.2 G: Advantages and Disadvantages of PVD for Internal Diameters

Advantages	Disadvantages
Very hard, wear resistant	Vacuum complexities
Smooth coating	Expensive
Good adhesion	Not suitable for rebuilds
	Through holes only
	Slow deposition rate
	Ion cleaning essential but difficult

Two European research teams (Hurkmans, et al. 1999; Hurkmans, et al. 2003) have investigated the use of PVD coatings as an alternative to electroplated hard chromium. Some of the coating materials include chromium nitride (CrN), diamond like carbon (DLC), carbide forming metals (Me-C:H), molybdenum disulfide (MoS_2) and titanium nitride (TiN). CrN has the advantage that it can be deposited in a layer up to 50 µm thick (for example, as a coating for piston rings), unlike some the other coatings which typically are quite thin.

Their assessment indicates that PVD coatings – including those that use a combination of materials with different characteristics (such as CrN and MoS_2) -- have potential for specific applications where a hard, corrosion resistant surface with low friction is required. Uses that they mention are automotive parts (e.g. high pressure fuel injection systems, turbo compressor shafts), punching and forming tools, and molds and dies.

CVD – Chemical Vapor Deposition

In chemical vapor deposition (CVD) reactant gases (typically diluted with inert gases) at room temperature enter a chamber and are heated or passed over a heated substrate. Gases contain the desired coating materials in vapor phase. As the reactants are adsorbed onto the surface of the substrate, decomposition and chemical reactions with the substrate forms the coating. Byproduct gases are then removed from the chamber.

Unlike PVD, CVD is not a line of sight process, so it is appropriate for complex geometries, such as blind holes. Similar to PVD, there are many process variations that enhance or modify the performance of CVD. Plasma enhanced CVD (PECVD) adds a plasma to the process which allows for a lower substrate surface temperature than CVD. Because the substrate doesn't need to be heated as much, it is applicable to a broader range of materials. Additional advantages include higher deposition rates and improved control of film properties.

An advantage of CVD is that it can deposit a uniform coating on complex shapes, can be used for a variety of coating materials, and a high deposition rate. Disadvantages include the high temperatures involved, which limits its use where substrates may deform under heat, the difficulty in accommodating large parts, and the many variables to be controlled in the process (Mattox 1999). Legg notes that the major application for CVD is thermal and barrier coatings (Legg 1999).

Trivalent Chromium Plating

Technical assessment of the CM-ECD Faradaic™ process was conducted with EPA funding by Faraday Technologies, the developer of the method. The results were sufficiently favorable for EPA to fund a second phase of the project involving implementation trials with businesses at different points in the supply chain: chemical vendors, equipment suppliers, fabricators, repair facilities, and original equipment manufacturers (NTTC, n.d.) The full report for that phase, which included tests by the United States Navy, has not been made public because it contains confidential business information.

The process developers note several additional technical advantages of trivalent chromium plating baths:

- They are not sensitive to current interruptions;
- Drag-in of chloride and sulfate from previous plating operations do not upset the catalyst balance;
- Cr(III) has better throwing power than Cr(VI).

They also assert that the charge modulation used in their process reduces the evolution of hydrogen during plating. This increases current efficiency, lowers the amount of energy required for plating, and reduces the risk of hydrogen embrittlement or hydrogen bubble inclusion in the plating. (Renz et al. 2003)In pilot stage testing, a variety of materials plated with the trivalent CM-ECD process were compared to traditional hexavalent chromium plating. Parameters that were measured included chromium thickness, plating efficiency, plating rate, hardness, and cost.

Using the Vickers hardness test (which is used to compare the hardness of metals, on a scale of 0 to 6000 kg/mm), trivalent and hexavalent chromium plated rods exhibited approximately equivalent results. In the first test, two Cr(III) treated rods had hardness values of 772 and 777, versus 772 for the Cr(VI) plated rod. In a second test where the plating variables were changed slightly, the two Cr(III) plated rods had values of 873 and 805, with the Cr(VI) rod at 825.

The trivalent process showed better results than the hexavalent chromium process in terms of plating rate and efficiency. The average plating rate for the CM-ECD process was 80 μm/h, as opposed to a rate of 135 μm/h for a hexavalent bath. Similarly, CM-ECD had a plating (current) efficiency of 24%, in comparison to a 30 % rate for the Cr(VI) process. (USEPA NCER, n.d.)

Financial Assessment

Thermal Sprays

Factors that must be considered when evaluating the switch from hard chrome plating to HVOF include the usual items in a direct comparison:

Processing Costs -- Power Costs, Fuel Costs

Consumable Costs -- Powders, fuel, equipment part repair/replacement

Labor Costs -- Processing/turn-around Time

Capital Costs -- Capital Equipment/depreciation; capital improvements such as soundproofing, equipment housing, etc.

Additional factors may be more difficult to quantify, but also are important:

Environmental compliance

One analysis shows that many cost/benefit analyses do not consider key environmental costs such as building/operating wastewater treatment plants, environmental compliance office costs or equipment depreciation (Legg 2005).

Health and Safety Compliance

The Surface Finishing Industry Council estimates that the costs for compliance with the OSHA PEL for hexavalent chromium of 5 μg/m^3 TWA will be extensive. The capital and annualized operating costs for existing hard chrome plating installations to comply with the PEL are estimated at several hundred thousand dollars. These costs include capital costs to install ventilation systems and operating costs for power, consumables, monitoring, testing, training, personal protective equipment, etc. (Richter, Hannapel 2005).

Improvements in product quality

HVOF coatings have shown improved product quality in many cases, which may reduce the amount of rework/replacement costs associated with these parts in the future. In one case, Luftansa Airlines has been able to increase the service life of hydraulic seals from ~1,000 flight cycles to >4,700 (Nuse, Falkowski 2000).

A detailed cost/benefit analysis (CBA) was conducted using the Environmental Cost Accounting Methodology (ECAM) at a landing gear overhaul facility that processes more than 1000 components per year. The results showed an annual cost avoidance of approximately $200,000 and a 15-year net present value (NPV) of approximately $1,800,000. The payback period on the $700K initial capital investment was 3-5 years (Anonymous 2004).

The table below shows cost comparison for a facility that processes 1,500 parts 4 in. in diameter and 36 in. long. This analysis was prepared by the Joint Service Pollution Prevention Team (Anonymous 2003).

Table 6.4.2 H: Cost Comparison of HVOF and Hard Chrome Plating

Factor	HVOF	Hard Chromium Electroplating
Capital and Installation	$250,000	$0
Operational Costs		
Powder/Plating	$60,000	$375,000
Gas	$21,600	$0
Labor	$45,000	$76,500
Rinsewater Treatment	$0	$500
Waste Disposal	$0	$1,000
Annual Total (without capital expense)	**$126,000**	**$453,000**

Weld Facing Methods

Legg (2004) estimates the cost of an electrospark alloying machine to be approximately $25,000. Because the process is most often used for small, localized repairs of parts, the cost of material is unlikely to be a major factor in selected this method. The machine is portable, so one unit can be used for on-site repairs throughout a facility.

It should be noted that in some cases the alternative to using this process would be to replace the part. Legg gives an example of a damaged compressor shaft with a value of $47,000 where ESA repair would be an alternative to replating or replacing the part.

Heat Treatments and Plasma Nitriding

Auf dem Brinke and Krug (Auf dem Brinke, T., Krug 2001) assert that their company's plasma nitriding plus oxidation process (IONITR OX) can result in production cost savings of 30-60% over hard chrome when used for automotive parts. They also state that the part-life of nitrided parts can be up to three times that of hard chrome plated parts.

Nanocrystalline Coatings

The SERDP study (McCrea, Marcoccia & Limoges 2003) compared the costs for hexavalent plating, conventional nickel plating, nanocrystalline cobalt, and nanocrystalline cobalt-3%phosphorus (Table 6.4.2 I). Only the plating cost and energy cost were included; environmental and production costs were not quantified.

Table 6.4.2 I: Cost Comparison of Hard Chromium Electroplating and Nanocrystalline Coating Processes (McCrea et al. 2003)

Plating Process	Nominal Plating Efficiency	Consumables	Relative Plating Cost (by weight)	Relative Power Cost (by weight)	Total Relative Process Cost
Chrome(VI)	25	Cr_2O_3	1.00	1.00	1.00
Nano Co	>90	Co	1.83	0.08	1.09
Nano Co-3%P	>90	Co, H_3PO_3	2.21	0.08	1.31

The cost of consumable materials for the hard chrome process was less than for the nanocrystalline processes. The amount of power needed for the chromium plating was much greater, however, partially balancing out the material costs. It should be noted that this study used a price for cobalt of $7/lb., and an energy price of $0.10 per kilowatt hour.

Vapor Deposition Methods

Physical vapor deposition (PVD) equipment has a high capital cost. One source (JSPPOH 2003) estimates the cost of installing a new PVD set-up at several hundred thousand dollars. The cost of operating PVD equipment is similar to electroplating, although waste-related costs are likely to be less.

Trivalent Chromium Plating

The CM-ECD Faradaic™ trivalent process has not yet been implemented at a commercial scale. Based on the pilot testing, costs associated with it should be equivalent or less than for hexavalent chromium plating. In 1999-2000, the cost for Cr(III) plating chemicals were about $5.33 per pound of chromium; Cr(VI) chemicals were around $4.61 per pound of chromium. Waste treatment, ventilation, and energy costs (as reported by one of Faraday Technologies' commercial partners) were less than those associated with hexavalent chromium plating.

Environmental Assessment

As noted earlier, a number of different materials may be used in most of these processes, depending on the nature of the end use. Consequently, an in-depth environmental and human exposure assessment for all the possible combinations of chemicals and processes is beyond the scope of this study. The following sections provide an overview of some the key issues for which there is published information.

Thermal Sprays

The pre-processing of parts for the application of HVOF coatings is fundamentally similar to that for hard chromium plating – the parts must be free of grease, oil, dirt and other contamination. Materials (such as solvents) used to clean the parts may have adverse environmental impacts.

Hard chrome plating results in two forms of hexavalent chromium waste: liquid wastes from rinsing and solution contamination, and air-borne hexavalent chromium emissions. Wastewater treatment and air emission scrubbing are generally used to mitigate these environmental exposures, but in both cases low amounts are allowed to be emitted to sewers and the atmosphere.

Inefficiencies in HVOF occur as overspray or bounce-back. Overspray occurs when the spray gun is not oriented directly at the part. Bounce-back occurs when the coating particles hit the surface of the part but do not adhere. It is estimated that ~35% of the material put into process does not become part of the coating. Overspray and bounce-back may be collected in ventilation/filter units and recycled for coating powders that have cost-effective metal contents. In some cases, the material may need to be disposed of as hazardous waste or solid waste, depending on the specific constituents.

The fuel and electrical power usage comparisons would need include several elements:

- Heating of chrome plating tanks
- Power used for solution agitation
- Electrical Current for the plating operation
- Energy usage for hydrogen embrittlement relief baking
- Power used for ventilation/scrubbing units (both coating methods)
- Air tempering of make-up lost to ventilation (both coating methods)

- Fuel use of HVOF equipment

The elimination of hard chrome plating solutions eliminates the risk of catastrophic tank failure with potential releases to the environment, or failure of wastewater treatment or air scrubbers, resulting in higher emissions of hexavalent chromium to the atmosphere.

Weld Facing Methods

There are unlikely to be significant environmental impacts from electrospark surface deposition (ESD). The technique is used for small areas, with small amounts of alloying filler metals being bonded to the part under repair. Waste products are minimal to none.

Heat Treatments and Plasma Nitriding

These processes may require cooling water. Some facilities (Anonymous 1996) extract the heat from the cooling water and use it in the facility heating system.

Nanocrystalline Coatings

The SERDP study (McCrea, et al. 2003) makes some general statements about environmental impact from the Co-P nanocrystalline process. It says that the waste stream volumes from the method are likely to be similar to those from hexavalent chromium plating. However, the materials used are not currently on EPA lists of hazardous chemicals, so the impacts from waste disposal should be less. The nanocrystalline process also is more efficient, and therefore uses less energy.

Vapor Deposition Methods

Chemical vapor deposition (CVD) can involve the use of precursor materials that are hazardous (*e.g.*, silane), and it also generates waste gases that must be collected. The chamber also needs periodic cleaning; fluorinated gases (greenhouse gases) may be used for this.

Trivalent Chromium Plating

Trivalent chromium baths produce much less hydroxide sludge than hexavalent chromium baths. This is due to the lesser concentration of chromium in the Cr(III) bath. The Cr(III) bath also does not need additives, so rinse water can be recycled without treatment (Renz et al. 2003).

Human Health Assessment

Thermal Sprays

For the most popular coating materials, tungsten carbide/cobalt, cobalt powder is the primary hazard. International Agency for Research on Cancer (IARC) classifies cobalt as a Group 2B material, possibly carcinogenic to humans. Hexavalent chromium is an IARC Group 1 material known to be carcinogenic to humans. Other HVOF coatings may contain metallic chromium, copper and other metals.

The OSHA PEL for Cobalt is 0.1 mg/m^3, versus 5 $\mu g/m^3$ for hexavalant chromium. The HVOF operation is typically carried out in an enclosure with particulate filtration; there should be no exposure of the operators to the coating material during spraying.

Exposure to powders may occur during handling of the powders to prepare them for spraying, during clean out of equipment, or spraying outside of an enclosure. Grinding of the coating will also create airborne particulates. Proper PPE should be worn to prevent exposure. One MSDS recommends supplied air respirators for these activities.

There is some question as the particle size distribution of the airborne coating. Particles less than 2.5 µm in diameter (PM 2.5) may be created. If this is the case, finer filtration may be required to prevent exposure to the coating materials (Legg, et al. 2001).

The American Welding Society has produced a safety and health fact sheet for thermal sprays (American Welding Society 1998). It notes that chlorinated hydrocarbon solvent vapor should not be present in areas where thermal spraying is being done, as dangerous phosgene gas can be produced if they are exposed to ultra-violet radiation. The ultra-violet and infra-red radiation that is involved with thermal spraying also has the potential to cause eye damage and skin burns.

Thermal spraying processes are very noisy, and generally are conducted in sound-proof booths. HVOF spraying can generate noise levels as high as 150 dBA (American Welding Society 1998).

Weld Facing Methods

Weld facing methods involve the use of welding equipment. Worker safety measures typically associated with welding (such as appropriate eye and respiratory protection) would be necessary. In addition, if the part being repaired contains stainless steel or a chromium coating, Cr(VI) fumes can be produced. Electrospark Deposition generally is used on a small scale, so risks are likely to be less than for traditional welding. Safety measures associated with the use of a laser are appropriate.

Heat Treatments and Plasma Nitriding

Very little has been published on human exposure concerns relative to these technologies. Plasma nitriding is considered safer than traditional nitriding because it does not use ammonia in the process.

Nanocrystalline Coatings

During the SERDP study (McCrea, et al. 2003) air emissions were sampled above the plating tanks for each of three electrolyte solutions: Co, Co-P, and Co-Fe-P. The samples were tested for cobalt, iron, chloride, sulphate and additives. The samples were taken about one inch above the plating solution surface, at a rate of 100mL/min, over a 5 hour period during plating. Table 6.4.2 J shows the results of the testing.

Table 6.4.2 J: Emissions Measurements for Co, Co-P and Co-Fe-P Baths

(McCrea et al. 2003)

Element/Compound	Toxicity Level[1] (mg/m³)	Bath #1 Cobalt (mg/m³)	Bath #2 Co-P (mg/m³)	Bath #3 Co-Fe-P (mg/m³)
Cobalt	0.05	0.0039	<0.0005	<0.0005
Iron	1.0	<0.0005	<0.0005	<0.0005
Chloride	N/A	0.216	0.043	0.053
Sulphate	N/A	0.258	0.014	0.29
Additive #1	N/A	N.A.B.	N.A.B.	N.A.B.
Additive #2	N/A	N.A.B.	N.A.B.	N.A.B.

[1] OSHA Time Weighted 8 Hr. Average N.A.B. = Not Above Background

Vapor Deposition Methods

Objects being coated using physical vapor deposition must be thoroughly clean and grease-free in order for the coating to adhere properly. Solvents used in the pre-cleaning of parts have the potential to be hazardous. Cleaning of the chamber to remove accumulated deposits sometimes is done by sand blasting, which can generate dust and particles. Chemical vapor deposition involves the use of several hazardous materials: carbon monoxide gas, hydrogen gas, hydrochloric acid and liquid chlorides (e.g. titanium chloride, vanadium chloride) (Midtgard, Jelnes 1991).

Trivalent Chromium Plating

Trivalent chromium plating has significantly fewer potential human health effects than hexavalent chromium plating. Cr(III) is not know to be carcinogenic, while the carcinogenic properties of hexavalent chromium are well-established. The TLV-TWA for trivalent compounds is 0.5 mg/m^3; for water soluble hexavalent compounds, it is 0.05 mg/m^3, and for insoluble compounds it is 0.01 mg/m^3 (American Conference of Governmental Industrial Hygienists (ACGIH) 2006).

Table 6.4.2 K: Summary Assessment of Alternatives to Hard Chromium Electroplating of Industrial Components

Factor		Cr(VI) Plating (Ref.)	Thermal Sprays	Weld Facing Methods	Heat Treatments & Plasma Nitriding	Nano-crystal-line Deposits	Vapor Deposition Methods	Functional Cr(III)
Technical and Performance Criteria	Wear Resistance	Very good	+	+	+	-/=	+ (CrN)	=/+
	Hardness	800VHN	+	+	=/+	-/=/+	+	=/+
	Impact Resistance	Poor	=	?	+	?	+	?
	Non-Line-of-Sight Plating	Yes	No	?	Yes	Yes	Yes (CVD) No (PVD)	Yes
	Hydrogen Embrittle-ment	Poor	+	?	+	+	+	?
	Corrosion Resistance	Moderate	+	N/A	+	+	Varies	=
	Smoothness	Requires grinding	=	=	?	+	+	=
	Fatigue Strength	Poor	+	=	?	?	?	?
	Deposition rate	Slow	+	?	?	+	+	?
Human Health Criteria	Carcinogenic	Yes	+	+	+	+	+	+
Environmental Criteria	Volume of waste generated	Significant	+	+	+	+	+	+

Comparison Key + Better = Similar - Worse ? Unknown

6.4.3 Passivation of Zinc Plated Parts and Zinc Galvanized Steel

Existing Process Overview

Passivation refers to a surface treatment that provides resistance to corrosion in which the protection is afforded by a film or thin coating that interacts with the underlying metal. Hexavalent chromium is a standard passivating chemical for zinc and zinc-alloy plated parts, and zinc galvanized steel. It slows the formation of white corrosion/white rust (zinc oxide) and subsequent oxidation of the underlying metal (typically steel).

In the process that uses hexavalent chromium, zinc plated parts are dipped into a tank containing a chromate salt such as sodium dichromate, along with other chemicals such as nitric acid, chromic acid and fluorides. The acidic solution reacts with the zinc plating to form a complex film that consists of zinc chromate and other chromate compounds in both the trivalent and hexavalent state. This is referred to as a "conversion coating" because the hexavalent chromium solution converts the surface to zinc chromate. The hexavalent chromium reacts with the metal, forming an inert trivalent chromium layer with "releasable" hexavalent chromium ions that inhibit corrosion (The Ohio State University 2005). The residual hexavalent chromium in the film will repassivate any areas on the surface that become compromised due to chemical or mechanical damage to the area – this property is referred to as "self-healing" (Wynn, Bishop 2002).

The conversion coating provides corrosion protection to the zinc plated parts. The color of chromated zinc varies according to the chemistry of the coating solution and the thickness of the coating. The thinner films are usually blue in color, with thicker coatings being yellow, and the thickest coatings being brown, olive or black (Eppensteiner, Jenkins 1999).

Table 6.4.3 A: Desirable Performance and Cost Characteristics of Hexavalent Chromium Passivates

(Wynn and Bishop 2005)

• Prevents Oxide Formation • Provides Color • Slows corrosion in prototypic tests (e.g. salt, spray) • Provides adhesion for organics (e.g. paint) • Helps prevent corrosion of painted surfaces (e.g. creep) • Conductive • Thin	• Flexible • Lubricious • Easily applied • Durable • Resilient (repairs itself) • Coats in recesses • Easy to strip • Inexpensive equipment • Single tank • Inexpensive chemistry

Description of Alternatives

Three alternatives were selected for study: molybdates, trivalent chromium compounds, and mineral tie-coat. A fourth alternative, the combination wet-dry-wet-dry process, was dropped from consideration because insufficient information on it was available.

Molybdates

Molybdate-based coatings inhibit corrosion by forming a protective oxide layer on metal. Solvent-based molybdate coatings most often contain zinc molybdate or zinc phosphomolybdate, while water-based molybdate coatings generally use calcium molybdate or calcium zinc molybdate (Simpson 1997). Sodium molybdate also may be used. A common brand name for molybdate corrosion inhibitors is Moly-White®. The molybdate-based chemistry can be added to various coating systems such as such as acrylic latex or alkyd paint, depending on the needs of the end user.

Trivalent Chromium Compounds

There are a number of types of trivalent chromium-based passivates, including trivalent blue, trivalent iridescent/green, low-temperature iridescent, and trivalent black. They vary in appearance, performance characteristics, thickness of the coating, the additional metal or metals that are used in the bath, and the temperature at which they are applied. Typically, the blue color is characteristic of a thinner film, and the iridescent and/or green color is a thicker layer.

The way in which the zinc plated or galvanized metal is treated here is similar to the process using hexavalent chromium Zaki (2002) describes the steps in a typical process, using "conventional plating lines": zinc or zinc alloy plate; rinse; activate with dilute acid; trivalent chrome passivate; optional drag out rinse; counter-current flow rinse; dry; seal and/or topcoat; and dry.

Sealers and topcoats are used to affect the color of the coated part, increase corrosion resistance, and improve lubricity and torque-tension properties. Sealers have a film thickness of 1-2 µm; topcoats are thicker, typically 4 µm or more (Bishop et al. 2003).

Mineral Tie-Coat

The mineral tie-coat process is a patented method of applying a thin mineral film on the surface of metal parts to inhibit corrosion and improve temperature resistance, flexibility, coating adhesion, and chemical resistance. It involves pretreating the material to be coated in order to clean and condition the surface, immersing it in a bath that contains a sodium silicate solution (which may contain various additives), and then electrodepositing the mineral coating with low voltage and current. The reaction between the coating and the metal surface forms a new protective surface. The process also is called cathodic mineralization, and is trade marked by Elisha Technologies as Elisha Mineral Coat (Elisha®EMC™). A topcoat or sealer may be used in conjunction with this process (Heimann 2001).

Technical Assessment

Key performance criteria for passivation of zinc include corrosion resistance, heat resistance, and appearance.

The test most often used for evaluating the corrosion resistance of passivation films is the neutral salt spray (or fog) testing, specified as ASTM B117. It involves subjecting the test material to a 5% neutral pH (6.5 to 7.2) sodium chloride solution for a specified length of time (depending on the performance requirements for the coating) at a controlled temperature. The test has some known limitations (for example, materials tend to corrode more quickly in actual marine conditions than under test conditions) (Baldwin and Smith 1999), but it is generally accepted as a way to compare different coatings (Wynn and Bishop 2005). Alternative methods for testing corrosion resistance include Electrochemical Impedance Spectroscopy (EIS), the Prohesion/QUV[11] test, humidity test, immersion test and the GM9540P Accelerated Corrosion Test developed by General Motors. In all cases, the coating is visually inspected for white rust formation, which indicates oxidation of the zinc surface, and red rust, which indicated oxidation of the steel substrate.

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[11] The test incorporates UV/condensation cycles with wet/dry salt-spray cycles.

Torque tension testing, which is used to evaluate repeatable clamp force, is done using a method employed by the automotive industry called USCAR-11. Torque tension is a key criterion for fasteners, such as bolts and screws (Donohue and Simpson 2003).

Much of the available information on testing of alternatives to hexavalent chromium for passivations has been conducted by scientists associated with the manufacturers of various chemical products. To the extent that this research has been published or presented at public conferences, it has been available for public review; however, much of it has not appeared in peer-reviewed journals. In the following sections it will be noted when the source of information is affiliated with a manufacturer or vendor.

Molybdates

There have been several studies by scientists in Europe, Asia and South America of the effectiveness of molybdate mixtures in preventing the corrosion of zinc and zinc galvanized steel. The consensus of these studies is that molybdates do protect against corrosion, but do not perform as well as hexavalent chromium passivations.

Magalhães et al. (2004) compared chromate treatment of electrogalvanized steel with a variety of sodium molybdate treatments. Variables included bath temperature, length of treatment, pH, type of acid used to adjust the bath pH, and additives. Using a long-term immersion test (in a Na_2SO_4 solution) the best of the molybdates (0.3 M molybdate acidified with H_3PO_4 to pH 3.0, at room temperature, 10 min treatment time) had a time to white rust of 21-22 d, compared to 27-28 d for the chromate control. Untreated samples corroded within 3-4 d (Magalhaes, et al. 2004).

A group of scientists in Portugal (Almeida et al. 1998) looked at the structure and performance of several alternatives to chromates: molybdates, tungstates, permanganates, and vanadates. Sodium molybdate outperformed the other chromate alternatives in a salt spray cabinet test, with its time to white rust (7 h), first red rust (75 h), and 10% red rust (85 h) being two to three times that of the other substances. However, the chromated comparison sample was superior in this test, with first red rust appearing at 340 h, and 10% red rust at 350 h. The molybdate did provide a better surface for paint adhesion than the chromate.

In a second phase of that study, the structure of the chromate and molybdate coatings was examined using scanning electron microscopy with energy X-ray dispersive spectrometry (SEM/EDS), X-ray diffraction (XRD) and X-ray photon spectroscopy (XPS) in order to investigate the possible reasons for the performance differences of the molybdate and the chromate coatings. The chromate conversion layer showed "…a fine and relatively regular structure, microrugous, with some pinholes and rich in chromium and zinc. Such a structure is … a result of a dehydration mechanism, which occurs during drying time, by volume retraction." In contrast, the molybdate layers "…revealed little zinc in the surface… showed a black-brown homogeneous color…and an amorphous and compact structure, more or less cracked, revealing a significant retraction after formation" (Almeida, et al. 1998).

The authors suggest that the cracks in the molybdate layer allow salt spray to penetrate to the substrate. In addition, the chromium ions in the chromate layer provide significant corrosion protection. The smoother surface of the molybdate layer is the likely reason for its better paint adhesion (Almeida, et al. 1998).

In a European study, two commercial products (Actirox 106 and Shieldex CP-7394, zinc phosphate modified by molybdate and calcium ion exchange silica, respectively) were compared to strontium chromate paint. When the two products were combined, they showed better corrosion protection performance than either individually, and "approached" the performance of strontium chromate (Zin, et al. 2003).

Tang (1994) examined the performance of a molybdate/phosphate process in passivating zinc-plated parts. They concluded that the process was superior to a hexavalent chromium-based process at low pH, similar in an outdoor exposure and prohesion (accelerated weathering) test, and not as good in a neutral salt-spray test (Tang, et al. 1994).

The manufacturers of Moly-White® make a variety of claims in their literature about the characteristics of their products, but provide only visual results of testing, not quantitative information. The products are white in color, and generally "heat stable at temperatures incurred for baking finishes."

Trivalent Chromium Passivates

Trivalent chromium coatings differ in appearance from hexavalent chromium films. Thin trivalent coatings typically are blue, with thicker coatings being iridescent or greenish; traditional chromate coatings most often are yellow. For most applications, the issue of appearance (specifically, color) is a matter of user preference rather than of the performance of the passivate. In cases where a specific color is required, topcoats or sealers often can be used to get the desired effect.

The difference in performance between trivalent and hexavalent passivates is due to the lack of soluble hexavalent chromium compounds at the metal surface. In the presence of atmospheric humidity, the soluble hexavalent chromium will migrate to areas where the coating has been compromised, providing corrosion protection (Wyrostek and Wynn 2006; Zaki 2002, 492-501). Trivalent films are not self-healing, and require a sealer or topcoat to perform adequately.

In tests conducted by SurTec International, a purveyor of passivation systems, thin coats of (blue) trivalent chromium passivates on zinc did not perform as well as yellow hexavalent passivates in salt spray testing. In barrel plating, thick layer trivalent coatings (also called chromiting) were slightly worse or equal to hexavalent coatings; in rack plating the trivalent was slightly better or equal to hexavalent. Time to corrosion for zinc and zinc/cobalt was 300 h; for zinc/iron and zinc/nickel, time to corrosion ranged from 350 h to 450 h (Zaki 2002, 492-501). SurTec's tests of heat resistance indicated that trivalent chromium passivations were superior to hexavalent coatings. The hexavalent coatings started to fail quickly at temperatures above 55° C, while the trivalent films remained crack-free and retained much of their corrosion resistance up to 200° C.

Upton (2001), affiliated with Macdermid, Inc., describes the results of salt fog testing on zinc and zinc-iron electroplated substrates. Test panels showed the trivalent passiavate to perform as well or better than the hexavalent. In barrel plating, however, the trivalent films were inferior to the hexavalent. Upton suggests that this is due to the lack of self-healing properties of the trivalent material; barrel plating is likely to result in some damage to the materials being treated (Upton 2001, 68-71).

In examining the effect of various sealers and topcoats (silicate-type, organic clear lacquer, and silane-based) on the corrosion resistance of trivalent passivates, Upton found that any of the sealers/topcoats improved resistance to salt fog. The improved performance was most noticeable in the barrel plated test material, where the sealer increased the corrosion resistance of the trivalent-treated items to a level similar or better than the hexavalent-treated materials. Similar findings about the efficacy of trivalent chromium passivates with a sealant were made by Bellezze, et al (2002): trivalent chromium films followed with a sealer are more corrosion resistant than unsealed hexavalent chromium films (Bellezze, Roventi, and Fratesi 2002/6/17, 221-230).

Thiery and Pommier (2004) of Coventya SAS, a French chemical manufacturer, reported on tests of trivalent blue, trivalent thick layer, and trivalent thick layer with added silica nanoparticles. They noted that the blue and thick layer passivates were not self-healing, and that the effectiveness of the electrolyte bath deteriorated over time. The addition of silica improved heat resistance (Thiery, Pommier 2004).

Mineral Tie-Coat

The manufacturer of the mineral tie-coat process, Elisha Technologies, has worked with the U.S. Department of Defense (DoD) and the automotive industry in refining and testing the EMC™ process. The process is most applicable to barrel coating applications of small to medium-sized parts, such as fasteners (Donohue, Simpson 2003).

While individuals associated with Elisha Technologies have published a number of articles comparing the performance of its process with chromate conversion coatings, they contain very little quantitative information on testing – they generally feature photographs of sample materials after testing rather than numerical comparisons. According to the manufacturer, Elisha EMC™ with a topcoat improved the corrosion resistance of zinc by three to six times over a chromate conversion coating with a topcoat. The tie coat also is more heat resistant than the hexavalent chromium, retaining its corrosion resistant properties up to 400° C. In addition, Elisha claims that treated parts can be topcoated several months after treatment (unlike chromate coatings), and that the mineral tie-coat is more flexible than chromate and less likely to delaminate in secondary operations.

In torque tension testing done under the USCAR-11 protocol, Elisha Technologies found that the samples treated with the mineral tie coat had lower values with less variability than samples with a yellow chromate coating (2.56 n/15.4 vs. 5.57 n/33.4). This means that the Elisha EMC™ treated fasteners had less surface friction and were more consistent than the hexavalent chromium samples (Donohue and Simpson 2003).

One of the EMC™ systems, Elisha® 7201B, is approved by General Motors as a sealer for zinc nickel plating. The General Motors specification that the process meets is the revised GM 4205.

In an independent study (Aramaki 2001) that examined the use of a sodium silicate solution in preventing corrosion (sodium silicate is one of the components of the mineral tie-coat process), SiO_5^{2-} was found to be highly effective. It exhibited inhibition efficiency of up to 90%. That study did not compare it to chromate passivations.

Financial Assessment

As noted by Dr. John Sinko, technical director at Wayne Pigment Corporation, "The contemporary selection/qualification paradigm for corrosion inhibitor pigments concerns toxicity, efficiency, and price" (Challener 2005). The cost of an alternative is measured not just in the price of treatment, but also in how well it performs over time. In addition, the monetary and societal costs of using toxic products and in complying with environmental and health standards are significant factors.

Hexavalent chromium-based products traditionally have been the least expensive and most effective corrosion inhibitor products. However, increased awareness and concern about the environmental and health effects of chromates has resulted in industry trying to phase out such products. European Union (EU) Directives restrict the use of hexavalent chromium in vehicles and electronic products sold in EU countries. Consequently, the difference in cost between hexavalent chromium and the alternatives is not a major factor considered by manufacturers that wish to compete in the EU.

In addition, the specifications for particular uses are likely to be more important in selecting an alternative rather than the cost differential between the alternatives. For example, in marine applications resistance to corrosion from salt spray is a critical factor that affects ship safety. In some cases only certain alternatives can be applied to parts of particular types, limiting the feasible choices. Because of the number of factors that come into play when selecting a passivation process for a particular use, it is difficult to make a direct cost comparison of the alternatives.

Tang (1994) noted that factors such as labor and capital investment account for about 65% of the cost of a passivation process, with the remainder being the actual materials, energy, and waste disposal/processing. Their analysis indicated that a molybdate-based process would be similar to a hexavalent chromium process in terms of labor and capital, more expensive for chemicals and energy, and less expensive for waste processing (Tang, et al. 1994, 20-22).

A manufacturer of a molybdate, Moly-White®, has provided some cost information for that product (Simpson pers. com. 2006). The list price of the material, which is added to paint or other coatings, ranges from about \$1.50 -\$4.00/lb. At a use level of around 0.5 lb/gal, the Moly-White additive increases the cost of the paint by \$0.75 -\$2.00/gal. With a typical coverage of about 250 ft^2/gal, the molybdate cost would be around \$0.003 -\$0.008/ft^2.

Environmental Assessment

Molybdates

As mentioned earlier, molybdates are added to a variety of coating formulations for application. Many of the environmental impacts from use of this alternative will be due to the characteristics of the coating, rather than the molybdate additive. If a solvent-based paint is used as a vehicle for the molybdate, any adverse impacts of that formulation also would need to be taken into consideration.

Molybdates that are used most often in corrosion inhibitors include sodium molybdate, zinc molybdate, and calcium molybdate. Some molybdate-based products may also include zinc oxide, calcium carbonate, and/or zinc phosphate. Zinc oxide and zinc phosphate are classified under ESIS as R50/53: very toxic to aquatic organisms and may cause long term adverse effects in aquatic environment.

Molybdenum sewer discharge is regulated in some sewer districts, as it is a regulated contaminant in wastewater treatment sludge. If the molybdenum level is too high in the sludge, it cannot be used for composting, as it becomes harmful to plants and animals (New England Biosolids Case Study #3, 2001)

Trivalent Chromium Passivates

Like the process for trivalent electroplating, the trivalent chromium passivation process requires a set of several chemicals. For example, the SurTec 680 chromiting process uses three complementary formulations:

- Chromium nitrate, disodium oxalate, and cobalt-(II)-nitrate;
- Phosphoric acid ester, isododecan, mixture of C-12 isoparafine
- Oxalic acid and salts of oxalic acid.

All of these mixtures have the potential to contaminate ground water or surface water if spilled or discharged. The MSDSs warn that even small quantities pose a danger to drinking water, and that the product must not be discharged to a sewer system.

Mineral Tie-Coat

Sodium silicate solution, the main component of the mineral tie-coat process, is harmful to aquatic life (when undiluted) due to its high pH (11.3 +/-). It is not persistent and does not bioacculuate. If it is diluted it depolymerizes into dissolved silica. It is not classified as a hazardous waste (MSDS for N® sodium silicate solution).

Human Health Assessment for All Alternatives

Molybdates

Molybdates are added to a variety of coating formulations for application. Many of the human exposure concerns from use of this alternative will be due to the characteristics of the coating, rather than the molybdate additive. If a solvent-based paint is used as a vehicle for the molybdate, any adverse impacts of that formulation also would need to be taken into consideration.

Molybdenum compounds have not been identified as having significant human health concerns. However, zinc oxide, which may be a component in molybdate-based formulations, produces toxic fumes when heated to decomposition. It is associated with metal fume fever – a "flu-like illness" that results from inhaling zinc oxide fumes, generally during welding. (American Welding Society 2002) The PEL for zinc oxide is 5 mg/m^3 for fume and respirable dust, and 15 mg/m^3 for total dust. The IDLH level is 500 mg/m^3 (NIOSH Pocket Guide). Another component of some of the products, calcium carbonate, can result in eye and respiratory system irritation.

Table 6.4.3 B: Summary of MSDS Recommendations for Moly-White® Products

Products	Components	Worker Safety Recommendations
Moly-White 101	Zinc Molybdate Zinc Oxide	Safety glasses should be used. Use sufficient general area ventilation. NIOSH-MSHA approved dust/mist/fume respirator is required when dust levels of 10 mg/M^3 are exceeded or fume is produced. If material is heated above 700 degrees C, full protective equipment, including self contained breathing apparatus, should be used.
Moly-White ZNP	Zinc Molybdate Zinc Oxide Zinc Phosphate	
Moly-White MZAP	Calcium Molybdate Calcium Carbonate	
Moly-White 212	Zinc Oxide Zinc Phosphate Calcium Molybdate Calcium Carbonate Zinc Oxide	

Trivalent Chromium Passivates

Several of the chemicals used in trivalent chromium passivates are hazardous to human health. Chromium nitrate is a skin, eye and respiratory system irritant, and over the long-term can damage the kidneys and cause a skin allergy. (New Jersey Department of Health and Senior Services 2001) The PEL for chromium nitrate and all other chromium(III) compounds is 0.5 mg/m^3 , compared to the hexavalent chromium PEL of 5 μg/m^3 (NIOSH Pocket Guide). There is no evidence that chromium(III) chemicals are carcinogenic. Disodium oxalate and oxalic acid are corrosive and can damage the kidneys, mucous membranes, and central nervous system. The REL for oxalic acid is 1mg/m^3 (NIOSH Pocket Guide). Isododecan is flammable, irritates the skin and respiratory system, can cause pulmonary edema if aspirated, and depresses the central nervous system if the fumes are inhaled.

Mineral Tie-Coat

Sodium silicate solution, which is a component of the mineral tie-coat process, is alkaline and corrosive. It irritates the respiratory tract if the mist is inhaled and the eyes and skin if there is contact, and can burn the intestinal tract if ingested. When it dries it forms a glass film that can cut the skin. The MSDS for sodium silicate solution recommends that workers use a NIOSH-approved dust and spray mist respirator where spray mist occurs, and body-protecting protective clothing, gloves, and chemical goggles. It has not been shown to be mutagenic or carcinogenic. Sodium silicate is component of many steel cleaning solutions currently used in metal processing shops, so the incremental increase in silica exposure is likely to be very low.

Table 6.4.3 C: Summary of Alternatives for Passivation of Zinc and Zinc Galvanized Steel

Assessment Criteria		Cr(VI) (Reference)	Comparison Relative to Cr(VI)		
			Molybdates[12]	Trivalent Chromium	Mineral Tie-Coat
Technical/ Performance Criteria	Corrosion Resistance (time to white rust)	Very Good	-	-/=/+[13]	+ **(with topcoat)**[14]
	Heat Resistance	Poor	+	+	+
	Torque/Tension	Good	?	?	+
Environmental Criteria	Toxic to Aquatic Species	Varies – toxic to some species	Varies – chemicals used in some formulations are toxic to aquatic life	+	+
	Drinking water MCL	~1 ppm	**Varies**	=	+
	Carcinogenicity	EPA Group A IARC Group 1	+	+	+
Human Health Criteria	Occupational Exposure: PEL (8-hour TWA)	~ mg/m^3	+	+	+
	Skin Irritant/Sensitizer	Yes	+/=	-/=	=

Comparison Key + Better = Similar - Worse ? Unknown

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[12] This assessment is for the molybdate only, not the coating that it is applied in.

[13] Performance of trivalent chromium depended on thickness of coating, plating method, addtives and whether a topcoat was used.

[14] Not suitable for barrel plating

6.5 Summary and Conclusions

There are several oxidation (or valence) states of chromium, each with its own chemical characteristics. The most common forms are trivalent chromium -- Cr(III) -- and hexavalent chromium -- Cr(VI). Trivalent chromium compounds can be either naturally occurring or a by-product of industry, while elemental chromium and the hexavalent compounds nearly always result from industrial activity. Trivalent chromium is the more stable form, and trivalent chromium compounds generally have low solubility in water and low reactivity. Most hexavalent chromium compounds are soluble in water, and are strong oxidizers.

Chromium can provide manufactured products with hardness, shininess, durability, color, corrosion resistance, heat resistance, wear resistance, and decay resistance. For example, decorative chrome plating produces a hard, shiny, durable surface coating on items such as school furniture. Jet turbine engine parts rely on hard chrome plating to resist corrosion, high temperatures, and wear. Chromium-based pigments are valued for their vivid colors and resistance to weathering; they are commonly used in traffic paints for those reasons. Anti-corrosion coatings containing chromium compounds are widely used in marine applications, where their resistance to salt spray and their "self-healing" properties are important. In addition, the biocidal properties of chromium compounds are key to their use in wood preservatives.

Hexavalent and trivalent chromium compounds differ in their health and environmental effects, with the hexavalent form being far more dangerous. Short-term effects of hexavalent chromium exposure (for example, from chromic acid droplets or chromate dust) include eye irritation and respiratory irritation, sneezing, or sensitization; in high concentrations, acute inhalation can cause ulcers in the nasal septum. In sensitive individuals, inhalation of hexavalent chromium can cause an asthma attack. Long-term inhalation of hexavalent chromium is known to cause lung cancer. It also can result in damage to the nasal mucous membrane, perforation of the nasal septum, and asthma.

Inhalation (of fumes or mist) and dermal contact with hexavalent chromium compounds used by workers in industrial operations are the primary exposure routes. If soil is contaminated with hexavalent chromium, it is possible that it will be touched and/or swallowed (for example, by children playing in a contaminated area). In areas where there has been industrial pollution of groundwater, there is the potential for ingesting hexavalent chromium-contaminated drinking water from groundwater wells.

Workers, rather than consumers, have the highest risk of adverse health effects from hexavalent chromium exposure. The industries with the greatest risk of occupational exposure to hexavalent chromium are chrome electroplating, stainless steel welding, metal coating and painting, printing, textiles, leather tanning, wood preservation, and cement or masonry work. Inhalation risk may be from fumes (welding), mists or droplets (electroplating, spray painting.) A hexavalent chromium electroplating bath produces severe off gassing, resulting in the creation of a large amount of chromic acid mist at the surface of the plating tank. Dermal exposure can result from contact with fluids, such as those used in electroplating, or materials containing hexavalent chromium, such as wet cement (OSHA, 2006).

For many years the OSHA PEL for hexavalent chromium compounds in workplace air was 52 $\mu g/m^3$ (ceiling concentration). That level was challenged by a variety of groups as being too high to adequately protect worker health, and OSHA proposed a rule (under a court-ordered deadline) that would lower the PEL to 1 $\mu g/m^3$ (time-weighted average). The final rule, issued on February 28, 2006, set the PEL at 5 $\mu g/m^3$ (time-weighted average). The NIOSH REL is 1 $\mu g/m^3$. As a general rule, OSHA and NIOSH strongly recommend that all exposures to confirmed human carcinogens, such as hexavalent chromium, be reduced to the lowest possible level.

Cost may not be an important factor in evaluating hexavalent chromium alternatives since its severe toxicity is driving many manufacturers to adopt alternatives. For example, it is likely that the new PEL will be very difficult for many manufacturers to meet using traditional engineering controls such as local exhaust ventilation. In addition, EU directives are driving manufacturers to find hexavalent chromium-free alternatives.

Based on a review of stakeholder input, published research on environmental, health and safety issues, and the availability of alternatives, three general categories of use were selected as priorities for this study: decorative chrome electroplating, hard/functional chrome electroplating, and passivation of zinc. Decorative and hard chrome plating were selected because of the severity of the hazard that chromium poses to workers in the electroplating industry. Passivation of zinc was selected as being representative of chromate conversion coatings, which was of concern to stakeholders both because of the potential for worker exposure and because chrome remains in the hexavalent state in the finished product.

Decorative Chromium Electroplating

Only two alternatives to decorative plating with hexavalent chromium were identified: trivalent chromium electroplating and low temperature arc vapor deposition (LTAVD®) of trivalent chromium. The trivalent electroplating technique has many technical and process advantages over the hexavalent method ("hexchrome"), but traditionally has produced a plate with a pewter-like color rather than the shiny blue-white plate from hexavalent plating. Recent developments in the trivalent plating process, however, now make it possible to produce a trivalent plate with a "near hexchrome" appearance. LTAVD® is a proprietary vapor deposition process that can produce a plated surface that is similar or better than hexchrome in hardness and corrosion and wear resistance and is very similar in color. It requires completely new equipment and so is not a "drop-in" replacement for hexchrome.

The environmental and human health impacts of the two alternatives are much improved compared to hexavalent chromium electroplating.

Trivalent plating chemicals are more expensive than hexavalent plating chemicals, although that is likely to change as trivalent systems increase in popularity. The cost of chemicals, however, is offset by the greater efficiency of the trivalent process and greatly reduced disposal costs. Cost information for this process has not been published, although the process is being used by several major manufacturers of consumer hardware, indicating that it is commercially viable. A major operating cost would be energy, but waste treatment costs are likely to be minimal.

Hard Chromium Electroplating

Six categories of process alternatives to "hard chrome" plating were selected for study: thermal sprays, weld facing, heat treatment, nanocrystalline coatings, vapor deposition, and trivalent chromium plating. Surface coatings of various materials, typically other metals, alloys, and metal carbides or nitrides, can be applied using these processes. Coatings that may be used to replace hard chrome include those based on titanium, tungsten, cobalt, aluminum and silicon. All of the alternatives have the potential to offer equivalent or better performance compared to hard chrome plating, although several have some limitations in their application. For example, thermal sprays are a line-of-sight technique, so cannot be used on complex geometries, and weld facing is limited to the rebuilding of worn parts. There should be at least one alternative that can meet the technical requirements of each different hard chrome plating application.

Many of the alternatives require a significant capital investment, ranging as high as several hundred thousand dollars in the case of a vapor deposition system. On the other hand, the manufacturers of these systems claim reduced operating costs. For example, a detailed cost-benefit analysis performed for the application of the high velocity oxy-fuel (HVOF) system at a landing gear overhaul facility showed an annual cost avoidance of approximately $200,000 and a 15-year net present value (NPV) of approximately $1,800,000. The payback period on the $700K initial capital investment was 3-5 years.

As is the case with decorative chrome plating, all of the hard chrome plating alternatives offer significant environmental and human health improvements over hexavalent chromium electroplating.

Passivation of Zinc

Three alternatives to the passivation of zinc plated parts and zinc galvanized steel were assessed: molybdate-based coatings, trivalent chromium-based passivates, and the mineral tie-coat process. Several technical evaluations have concluded that molybdates do protect against corrosion, but do not perform as well as hexavalent chromium passivations. On the other hand, the molybdates offer better heat resistance than hexavalent chromium. Trivalent chromium coatings differ in appearance from hexavalent chromium films. Thin trivalent coatings typically are blue, with thicker coatings being iridescent or greenish; traditional chromate coatings most often are yellow. For most applications, the issue of appearance (specifically, color) is a matter of user preference rather than of the performance of the passivate, and topcoats or sealers often can be used to get the desired effect. Trivalent chromium compounds are not "self-healing" like hexavalent chromium, and require a sealer/topcoat in order to offer the same level of corrosion resistance. The manufacturer of the mineral tie coat process claims that it is equal to or better than hex chrome in corrosion resistance (with topcoat), heat resistance, and torque/tension performance.

Little cost information is available for these alternatives. One analysis indicated that a molybdate-based process would be similar to a hexavalent chromium process in terms of labor and capital, more expensive for chemicals and energy, and less expensive for waste processing.

All of the alternatives should offer significant improvements over hexavalent chromium in terms of their environmental and human health impact, although chemicals used in some molybdate formulations are toxic to aquatic life.

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Chapter 7. DEHP

Five Chemicals Alternatives Assessment Study

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7.1 Overview for DEHP

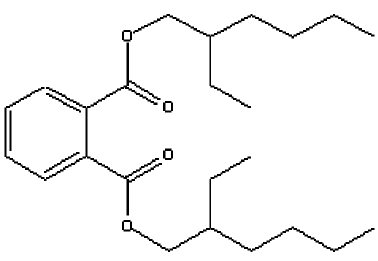
Plasticizers are additives to otherwise rigid plastics that impart the flexibility required for certain applications. Phthalates are a class of plasticizers that are commonly used in a variety of applications, from consumer products to medical devices to industrial equipment. They are organic chemicals produced from petroleum and are the most commonly used plasticizers in the world. Over 90% of the phthalates produced are used specifically for their plasticizing function, giving plastics, primarily polyvinyl chloride (PVC), strength, flexibility and durability. The purity requirements for commercial plasticizers are very high; phthalate esters are usually colorless and are mostly odorless. Although the various kinds of plasticizers in use today have some structural similarity, each one is different in the way it performs.

Phthalates are products of simple esterification reactions, which can be carried out readily in heated kettles with agitation and provision for water take-off. While some manufacturing facilities produce plasticizers by such batch methods, newer, highly automated plants operate continuously, particularly if they emphasize a single product. Esterification catalysts speed the reaction and are neutralized, washed and then removed. The reaction usually requires an excess of alcohol, which is readily recycled. Analogous syntheses yield aliphatic dicarboxylic acid esters, benzoates and trimellitates (Stanley 2006).

Di (2-ethylhexyl) phthalate (DEHP) is the international standard PVC plasticizer and properties of other plasticizers are usually reported relative to those of DEHP. As a plasticizer for PVC, DEHP generally offers excellent compatibility, desirable fusion properties and a set of performance properties that, for many uses, require little modification with other types of plasticizers.

The chemical structure of DEHP ($C_{24}H_{38}O_4$) is illustrated in Figure 7.1A:

Figure 7.1 A: Chemical Structure of DEHP



DEHP (CAS No 117-81-7) is also known as di-octyl phthalate (DOP) or bis (sec) ethylhexyl phthalate. It is the most commonly used phthalate plasticizer with an estimated annual production in Western Europe of 500,000 metric tons per year (Greens 2004) and an estimated global annual production of between 1 and 4 million metric tons per year (Swedish Chemicals Inspectorate (KemI) 2003). The U.S. production of DEHP was 120,000 metric tons in 2002. This represented 18% of the total U.S. consumption of phthalate plasticizers (Bizzari et al. 2003).

7.1.1 Characteristics

DEHP is a colorless liquid with almost no odor. It represents one of the most versatile and widely used plasticizers in industrial applications primarily because of its overall performance characteristics and its wide range of appropriate properties for a great many cost-effective, general purpose products (Phthalates Information Centre Europe 2005).

Table 7.1 A: Chemical/Physical Characteristics of DEHP (USEPA 2005)	
Melting/Boiling Point	-50°C / 230 °C
Vapor Pressure	1.32 mm Hg at 200 °C ($1.4\text{x}10^{-6}$ mm Hg at 25°C)
Octanol/Water Partition Coefficient	Log Kow = 4.89
Specific Gravity	0.99 at 20 °C
Solubility[15]	0.285 mg/L at 24 °C (slightly soluble in water)
Soil Sorption Coefficient	Log Koc = 4 to 5; low mobility in soil
Bioconcentration Factor	Log BCF = 2 to 4 in fish and invertebrates, Log BCF = 2.93 in fathead minnows; expected to bioconcentrate in aquatic organisms
Henry's Law Coefficient	$1 \text{ x } 10^{-4}$ atm-m^3/mole
Biodegradation	Half-Life in water = 2 to 3 weeks

7.1.2 Health and Environmental Impacts

Summary

DEHP is present in many products that require the use of flexible plastics. With a relatively low vapor pressure and water solubility, the amount of DEHP in plastic products that will be released is fairly low relative to the amount in products. The amount released is affected by the medium it is in. In non-aqueous environments (*e.g.,* fats) more DEHP will be released. Many studies indicate that the human body burden of DEHP has been increasing over the decades as flexible plastics find new uses. In addition, more recent studies that look at the presence of metabolites of DEHP excreted by humans provide supporting evidence that DEHP exposure to humans is in fact occurring. The following sections detail some of the more recent knowledge and generally accepted understanding of the health and environmental effects of exposure to DEHP.

Human Health Effects

Based on our current scientific knowledge, human exposure to DEHP during manufacture or consumer use occurs primarily through inhalation and oral exposure. There has been only limited study of dermal exposure to DEHP, but it is thought to be an insignificant mechanism for adverse human health effects. This is due to low absorption rate and limited human exposures through dermal contact. Exposure may also occur during medical fluid injection if DEHP leaches into the medical fluids as a result of direct contact with the DEHP-plasticized PVC materials used in some medical devices. When these fluids have high lipid content the likelihood of DEHP leaching into the fluids increases.

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[15] Other sources estimate water solubility as 0.00249 mg/L at 25°C (Staples 2003), which is several orders of magnitude lower than what is reported by EPA.

Information on the oral toxicity of DEHP in humans is limited to gastrointestinal symptoms (mild abdominal pain and diarrhea) based on the evidence of two individuals who ingested a single large dose of the compound (Agency for Toxic Substances and Disease Registry (ATSDR) 2002). Because of the dearth of scientific studies that have been conducted on humans, only limited information is available relative to the health effects of DEHP in humans following inhalation or dermal exposure, although recent studies are exploring the potential for effects (*e.g.,* asthma) associated with inhalation of dusts containing DEHP (Børnehag et al. 2004).

When DEHP enters the human body, the compound is rapidly metabolized into various substances that are more readily excreted. The first of these metabolites to be created is mono-ethylhexyl phthalate (MEHP), which is thought to be responsible for much of DEHP's toxicity. MEHP is primarily formed by the hydrolysis of DEHP in the gastrointestinal (GI) tract and then absorbed (Centers for Disease Control and Prevention (CDC) 2005). The enzymes (lipases and esterases) that break down DEHP into MEHP are found mainly in the GI tract, but also occur in the liver, kidney, lungs, pancreas, and plasma.

MEHP is subsequently further metabolized by different oxidation reactions, creating a number of other metabolites, the most significant of which include (Koch et al. 2006):

- 2-ethyl-5-hydroxyhexyl phthalate (5OH-MEHP)
- 2-ethyl-5-oxy-hexylphthalate (5oxo-MEHP),
- 2-ethyl-5-carboxy pentylphthalate (5cx-MEPP), and
- (2-(carboxymethyl)-hexyl) phthalate (2cx-MMHP).

These secondary metabolites of DEHP represent the majority of DEHP metabolites (approximately 70%) excreted in urine versus MEHP, which is present in urine at approximately 6% of the total amount excreted (Koch et al. 2006). 5OH-MEHP and 5oxo-MEHP are produced by the oxidative metabolism of MEHP and are present at roughly three-to ten-fold higher concentrations than MEHP in urine (Koch et al. 2003). Because the majority of conversion of DEHP to MEHP occurs in the GI tract, exposures to DEHP by ingestion may be more hazardous than by intravenous exposure, which largely bypasses the GI tract. The primary purpose of studying these secondary metabolites is that the long half-times of elimination of the carboxy metabolites (5cx-MEPP and 2cx-MMHP) make them appropriate parameters for measuring time-weighted body burden of DEHP, while 5OH-MEHP and 5oxo-MEHP appear to more accurately reflect short-term human exposure to DEHP (Koch et al. 2006). However much less is known about the potential human effects of exposure to these secondary metabolites.

The initial metabolism of DEHP to MEHP is qualitatively similar among mammalian species, so that animal studies are likely to be useful in understanding the consequences of human exposure. The similarity of secondary metabolite creation among non-human species is less well known. There are a number of animal studies that have been conducted over the past several decades looking at potential health effects associated with exposure to DEHP. The primary studies have involved rodents (rats and mice) while more recently studies have been conducted on primates (such as marmosets and cynomolgus monkeys) and pigs. Studies of rats represent the most prevalent source of information on potential health effects associated with varying doses and exposure routes. Studies of primates focused on common marmosets (Kurata et al. 1998) and cynomolgus monkeys (Pugh et al. 2000).

Cancer Risk

DEHP is currently classified by the USEPA as a Class B2 carcinogen. This determination is based entirely on liver cancer in rats and mice. In 2000 IARC changed its classification for DEHP from "possibly carcinogenic to humans" to a Class 3 carcinogen "cannot be classified as to its carcinogenicity to humans," because of the differences in how the livers of humans and primates respond to DEHP as compared with the livers of rats and mice (ATSDR 2002).

Reproductive/Developmental Effects

No studies are currently available that directly indicate reproductive effects in humans after oral exposures of humans to DEHP, but many animal studies of this potential have been conducted. Studies in rodents exposed to doses in excess of 100 mg/kg/day DEHP clearly indicate that the testes are a primary target organ, resulting in decreased testicular weights and tubular atrophy. Weights of the seminal vesicles, epididymis, and prostate gland in rats and mice are also reduced by oral exposure to DEHP (Gray and Butterworth1980; Lamb et al. 1987).

Studies suggest that nonhuman primates are less sensitive than rodents to the effects of DEHP on the degree and permanence of testicular damage (Kurata et al. 1998). Evidence suggests that MEHP might be the toxic metabolite in the testes. A review of various studies indicates that MEHP generally produces developmental, reproductive and hepatic toxicity in laboratory animals (ATSDR 2002). In one study, 1,055 mg/kg/day of DEHP administered for 5 days to rats did not affect testicular weight or structure, but an equimolar dose of MEHP had a significant effect (Sjoberg et al. 1986).

Based on current studies, and in accordance with the conclusions drawn by the NTP (ATSDR 2002), the developing organism is more sensitive to exposure to DEHP than the juvenile or adult organism. The age at first exposure to DEHP appears to have a clear influence on the degree and permanence of testicular damage (Gray and Butterworth 1980). Based on the multiple studies evaluated by the CERHR panel as part of its review of the reproductive toxicity of DEHP, they have determined that exposure of neonates to DEHP is a "serious concern" (National Toxicology Program Center for the Evaluation of Risks to Human Reproduction (NTP-CERHR) 2005).

While there was insufficient human data to directly demonstrate reproductive effects in human, the Panel concluded that animal data suggest there is sufficient evidence that DEHP causes reproductive toxicity in female rats (decreased numbers of corpora lutea and growing follicles), in female marmosets (increased ovary weight and uterine weight) and in male rats for exposures that included gestational and/or peripubertal periods (NTP-CERHR 2005). The recent update of the NTP study of the toxicological effects of DEHP indicates that DEHP is considered to be of serious concern when critically ill infants are exposed to products containing this chemical (NTP-CERHR 2005). In particular, the NTP Panel has serious concern that intensively medically treated male infants may experience adverse affects on their reproductive tract development and function.

As a result of its review of associated studies, the NTP has determined a LOAEL for exposure to DEHP of 38 – 144 mg/kg bw/day and a NOAEL for males of 3.7 mg/kg bw/day (*NTP 2005*).

Exposure Routes

The ATSDR has determined that because DEHP's effects are exerted in animals in a dose-related manner and exhibit threshold responses, and because concentrations of DEHP in the environment are expected to be well below the established effect thresholds, DEHP is not expected to pose a serious public health concern for the vast majority of the population (ATSDR 2002). It is important to note that this opinion was offered prior to the availability of pertinent studies of the potential for exposure to DEHP in dust found in indoor environments. Specifically, studies have identified a somewhat elevated presence of DEHP in household dusts in homes with DEHP/PVC surfaces such as flooring and wall coverings (Børnehag et al. 2005). While this and related studies are preliminary and do not clearly indicate associated health effects, they do suggest that the general public may be exposed to DEHP in indoor environments.

Because DEHP has a very low vapor pressure, little is found in air. DEHP molecules that are present in air will adsorb onto dust particles and will be deposited on surfaces through gravity, rain or snow. Indoor releases of DEHP to the air from plastic materials, coatings, and flooring in home and work environments, although small, can lead to higher indoor levels than are found in the outdoor air (Børnehag et al. 2005).

In its evaluation of the potential for reproductive toxic effects, the CERHR determined that there is some cause for concern relative to exposure of DEHP by the general population of infants and toddlers, and serious concern for neonates undergoing intensive medical treatment (NTP-CERHR 2005). The variation in level of concern is most closely related to the potential for exposure of sub-populations to have different weight-related doses due to body size and duration of exposure.

One of the primary routes of exposure to the general population is associated with the use of DEHP in flexible PVC medical devices. Parenteral[16] medical exposure to DEHP of critically ill infants has been shown to exceed general population exposures by several orders of magnitude. Numerous studies have been conducted to determine or estimate the exposure level of neonates and infants to DEHP due to various medical procedures. Figure 7.1B presents a compilation of human exposure data associated with a variety of common medical procedures, as presented in the report entitled "Preventing Harm from Phthalates, Avoiding PVC in Hospitals" (Ruzickova et al. 2004). In it, the mean and range of exposure levels of DEHP measured in various studies are summarized based on specific medical procedures. Based on these data, one of the primary potential sources of exposure on a body weight basis is extracorporeal membrane oxygenation[17] (ECMO) in infants.

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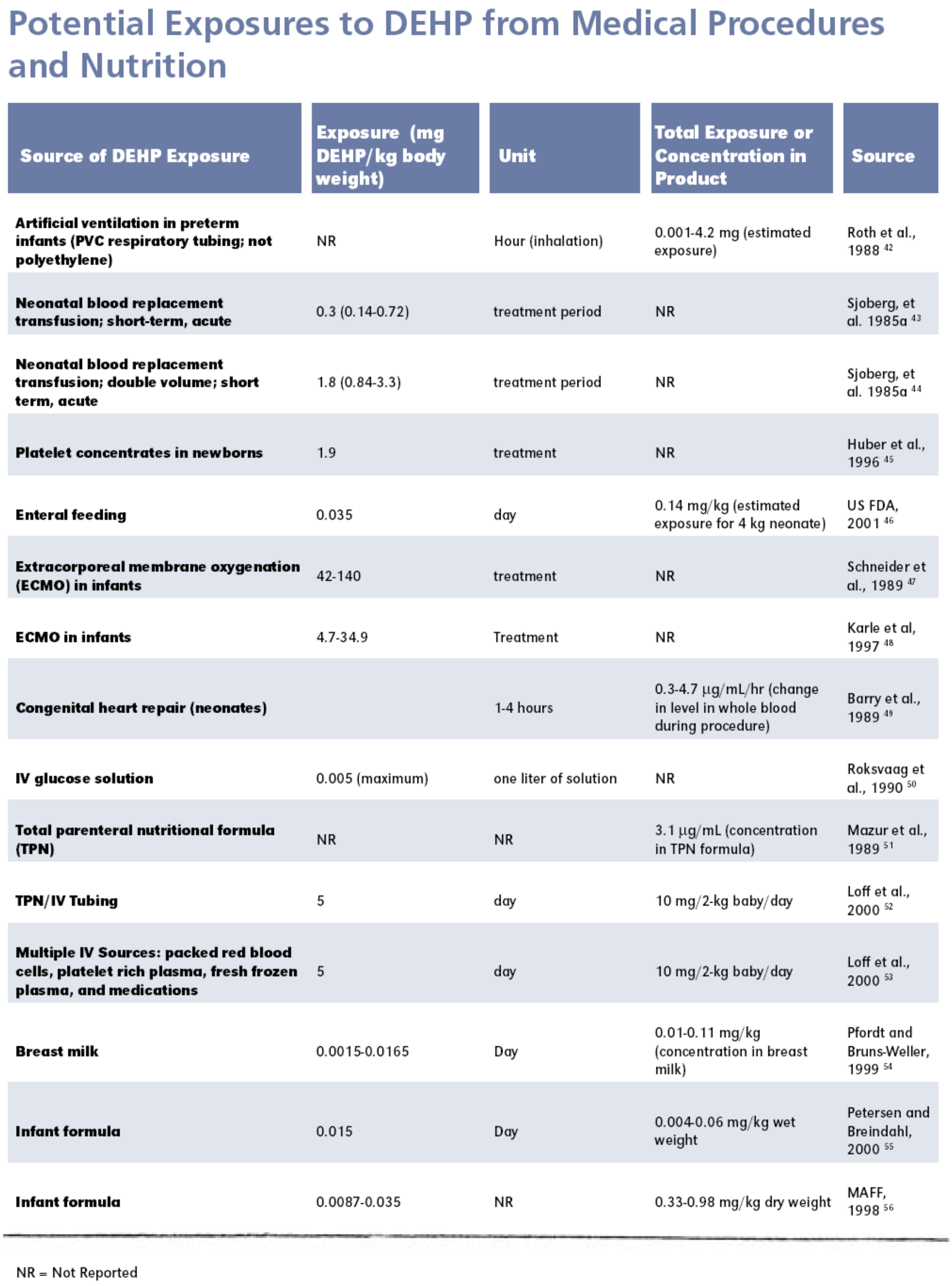
[16] Procedures where medical fluids are taken into the body in a way other than the digestive tract, usually subcutaneously or intravenously

[17] ECMO is used in infants who are extremely ill due to breathing or heart problems. The purpose of ECMO is to provide adequate oxygen to the baby while allowing time for the lungs and heart to "rest" or heal.



Potential Exposures to DEHP from Medical Procedures and Nutrition

Source of DEHP Exposure	Exposure (mg DEHP/kg body weight)	Unit	Total Exposure or Concentration in Product	Source
Artificial ventilation in preterm infants (PVC respiratory tubing; not polyethylene)	NR	Hour (inhalation)	0.001-4.2 mg (estimated exposure)	Roth et al., 1988 [42]
Neonatal blood replacement transfusion; short-term, acute	0.3 (0.14-0.72)	treatment period	NR	Sjoberg, et al. 1985a [43]
Neonatal blood replacement transfusion; double volume; short term, acute	1.8 (0.84-3.3)	treatment period	NR	Sjoberg, et al. 1985a [44]
Platelet concentrates in newborns	1.9	treatment	NR	Huber et al., 1996 [45]
Enteral feeding	0.035	day	0.14 mg/kg (estimated exposure for 4 kg neonate)	US FDA, 2001 [46]
Extracorporeal membrane oxygenation (ECMO) in infants	42-140	treatment	NR	Schneider et al., 1989 [47]
ECMO in infants	4.7-34.9	Treatment	NR	Karle et al, 1997 [48]
Congenital heart repair (neonates)		1-4 hours	0.3-4.7 µg/mL/hr (change in level in whole blood during procedure)	Barry et al., 1989 [49]
IV glucose solution	0.005 (maximum)	one liter of solution	NR	Roksvaag et al., 1990 [50]
Total parenteral nutritional formula (TPN)	NR	NR	3.1 µg/mL (concentration in TPN formula)	Mazur et al., 1989 [51]
TPN/IV Tubing	5	day	10 mg/2-kg baby/day	Loff et al., 2000 [52]
Multiple IV Sources: packed red blood cells, platelet rich plasma, fresh frozen plasma, and medications	5	day	10 mg/2-kg baby/day	Loff et al., 2000 [53]
Breast milk	0.0015-0.0165	Day	0.01-0.11 mg/kg (concentration in breast milk)	Pfordt and Bruns-Weller, 1999 [54]
Infant formula	0.015	Day	0.004-0.06 mg/kg wet weight	Petersen and Breindahl, 2000 [55]
Infant formula	0.0087-0.035	NR	0.33-0.98 mg/kg dry weight	MAFF, 1998 [56]

NR = Not Reported

Figure 7.1 B: Compilation of Various Peer-Reviewed Scientific Data Sources from the report "Preventing Harm from Phthalates, Avoiding PVC in Hospitals" June 2004 (Ruzickova et al. 2004)

In its 2002 report entitled "EAP on DEHP in Medical Devices MDB Report: An Exposure and Toxicity Assessment" (Health Canada 2002), the Medical Devices Bureau of Health Canada concluded that exposures of infants to DEHP occur as follows:

1. Infants undergoing routine replacement blood transfusions may be exposed to doses of DEHP 1-2 orders of magnitude above general population exposures. Infants undergoing intensive therapies may be exposed to levels up to 3 orders of magnitude above general exposures.
2. Infants receiving double volume exchange transfusion, which is the short-term procedure reported to give the highest acute exposure – up to 23 mg/kg body weight/day.
3. ECMO for infants, which is the sub-acute medical treatment that results in one of the highest daily DEHP exposures per kg body weight and the highest daily exposure over a prolonged period of time – up to 14 mg/kg/day during the 3 to 30-day treatment period.

Other medical procedures that result in very high exposures relative to the general population exposure include cardiac bypass procedures, total parenteral nutrition therapy, infusion of lipophilic drugs using PVC bags and tubing (which is contraindicated in the directions for use), and possibly, respiratory therapy.

Environmental Hazards

DEHP is not chemically bound to the PVC polymer matrix and can therefore be released throughout the lifecycle of polymer products. Release of DEHP to the environment potentially occurs not only during the production, distribution and incorporation into PVC but also when the PVC material is heated or comes into contact with certain media. Consequently, DEHP may be lost from the finished products during their use or disposal. In general this is a relatively slow process as indicated by common flexible PVC products' (*e.g.,* vinyl flooring) ability to maintain flexibility.

The half-lives of DEHP and of phthalates in general in the environment are relatively short. Phthalates typically spend hours in the atmosphere and months in soil. However, phthalates adsorbed to soil and sediments can persist in the environment for years. Although DEHP has a low bioconcentration factor, it will preferentially bioconcentrate in aquatic organisms rather than remain in water due to its low water solubility. However, DEHP does not significantly bioaccumulate in the food chain, nor is it expected to bioconcentrate in terrestrial organisms.

DEHP has a strong tendency to adsorb to soil and sediments. Experimental evidence demonstrates strong partitioning to clays and sediments (USEPA 2005). DEHP released to water systems will biodegrade fairly rapidly, exhibiting a half-life of 2 to 3 weeks.

DEHP enters the environment through releases from manufacturing facilities that make or use DEHP and from consumer products that contain it. Over long periods of time, it can also migrate out of plastic materials and into the environment. Therefore, DEHP is widespread in the environment; about 291,000 pounds were released in 1997 from industries (USEPA 2005). According to EPA, it is often found near industrial settings, landfills, and waste disposal sites. Based on the TRI report, a large amount of plastic containing DEHP is buried at landfill sites (USEPA 2005). When DEHP is released to soil, it usually attaches strongly to the soil and does not move very far away from where it was released. DEHP has also been found in groundwater near waste disposal facilities (USEPA 2005). When DEHP is released to water, it dissolves very slowly into underground water or surface waters that contact it.

DEHP can break down in the presence of other chemicals to produce MEHP and 2-ethylhexanol. Many of the properties of MEHP are like those of DEHP, and therefore its fate in the environment is similar. In the presence of oxygen, DEHP in water and soil can be broken down by microorganisms to carbon dioxide and other simple chemicals. DEHP does not break down very easily when deep in the soil or at the bottom of lakes or rivers where there is little oxygen.

7.1.3 Use and Functionality

As a plasticizer, the primary function of DEHP used in products is to soften otherwise rigid plastics and polymers, such as PVC. Most industry analysts agree that an estimated 90% of DEHP is used as a plasticizer for PVC. DEHP exhibits good gelation, plasticizing efficiency and adequate viscosity properties in PVC emulsions making it ideal for most plasticized PVC applications (Ecobilan 2001).

As a result of DEHP's plasticizing performance as well as its reasonable cost, DEHP is found in a wide variety of products in every day use. DEHP not only softens the PVC but enhances the color-fast, durable, low-maintenance qualities that make PVC desirable and useful in building materials, autos, toys, and medical devices. Table 7.1B presents a summary of information on the various uses of DEHP. Information about amounts used in products in the EU (and assumed to apply to the US) or manufactured in Massachusetts is provided when available.

Table 7.1 B: Survey of Uses of DEHP

Major Use Category	Uses/Applications	Used in Product in EU **	Used in Mfg in MA (lb/y)	Important Considerations
Polymer Uses	**Consumer Products**			
	Toys	(US producers generally no longer use DEHP)		Permanently banned in EU; Potentially vulnerable population exposed
	Sheet/Film (e.g. food contact)	15% of total use (for all sheet materials)	180,600 (otherwise used) 734,000 (incorporated into product)	FDA approved for applications not touching food.
	Vinyl Shower Curtain			Large consumer usage; ubiquitous
	Vinyl Wall Covering			Large consumer usage; ubiquitous
	Car Undercoating	1% of total use		Alternatives available
	Footwear	8% of total use		Alternatives available
	Upholstery			High consumer exposure potential; large usage; ubiquitous
	Medical Devices (approximately 25% of total US consumption of DEHP) (Bizzari et al. 2002)			
	Plastic sheet materials (e.g. bags)	15% of total use (figure for all sheet materials, not just medical devices)	566,300 (typically 20-40% DEHP)	High usage; Potentially vulnerable population exposed; Many alternatives possible
	Tubing (e.g. IV tubing)		minimal	High usage; Potentially vulnerable population exposed; Many alternatives possible
	Industrial/Commercial Uses (approx 45% of total US consumption of DEHP (Bizzari et al. 2002)			
	Resilient flooring (also residential uses)	15% of total use	1,049,500	Used in MA; High occupational exposure potential
	Roofing			
	Aluminum Foil Coating/ laminating			Alternatives available
	Paper Coating			Alternatives available
	Extrudable PVC Molds/Profiles	1% of total use	649,000	Used in MA
	Electronic Component Parts		58,600	Used in MA

Table 7.1 B: Survey of Uses of DEHP

Major Use Category	Uses/Applications	Used in Product in EU **	Used in Mfg in MA (lb/y)	Important Considerations
	Wire/Cable Coating/Jacketing	15% of total use	21,200 (manufactured) 70,000 (incorporated into product)	Used in MA
Non-Polymer Uses	Lighting Ballasts & Electric Capacitors			Minimal use
	Vacuum Pump Oil			Minimal use
	Perfumes/Cosmetics			Other phthalates used preferentially in this industry
	Pesticides			Little information on use
	Printing Inks (e.g. lithographic)	<1% of total use		Potential consumer exposure to printed films
	Paints & lacquers	<1% of total use		Potential occupational and environmental exposure
	Adhesives & Coatings	2% of total use	13,500	Used in MA; Potential occupational and environmental exposure
	Ceramics	<<1% of total use		Limited information on use

*** Based on 2003 KemI study of EU uses of DEHP in 1997 – assumed to apply in the US (KemI 2003).*
Note: if a cell is blank this indicates that no data is available

7.2 DEHP Use Prioritization

Chemical Uses

The uses of DEHP in Massachusetts manufacturing are presented based on the 2003 TURA data (Toxics Use Reduction Institute (TURI) 2003). Over 3.5 million pounds of DEHP were used in Massachusetts in 2003. Further details are outlined in Table 7.2A below:

Table 7.2 A: Total DEHP Use in Massachusetts in 2003

CAS	Chemical Name	TOTAL USE (lbs)	Generated as a Byproduct (lbs)	Shipped in/as Product (lbs)	Total Emissions
117-81-7	DEHP	**3,593,614**	320,631	3,260,296	3,300

Thirteen companies reported DEHP use in 2003 (TURI 2003). These include companies manufacturing various flexible PVC products such as flooring, molded products and medical devices, plastic compounders and chemical distributors. The company reporting the highest use of DEHP makes rubber and plastic commercial and industrial flooring products.

Uses in Products

TURI developed a list of products and/or applications where DEHP is used utilizing sources from both the EU and the US. Table 7.1B outlines the major known uses and applications of DEHP in products today. As shown, the primary products using DEHP for its plasticizer functionality include:

- Adhesives and coatings;
- Extrudable PVC molds and profiles (*e.g.,* bumpers for marine applications);

- Food packaging applications;
- Footwear (in soles and in PVC design appliqués);
- Medical devices (in a variety of bags and tubing devices);
- Resilient PVC-based flooring materials;
- Toys;
- Vinyl wall coverings (as part of the PVC emulsion used to provide water resistance); and
- Wire and cable coating and jacketing compounds.

In order to identify the priority uses of DEHP, a more comprehensive list of uses was presented to Massachusetts stakeholders, for their input (see Appendix B for this list of uses associated with DEHP). Stakeholders discussed the routes of DEHP exposure including oral exposure (*e.g.,* mouthing toys, film covering foods), inhalation (*e.g.,* off-gassing), dermal exposure, exposure from DEHP in dust, injection after leaching of DEHP into medical bag devices, etc.

Priority Uses

Table 7.2B summarizes the major uses of DEHP which were discussed with the stakeholders and their general comments.

Table 7.2 B: DEHP Uses and Stakeholder Discussion

Uses/Applications	Stakeholder Discussion
Consumer Products	
Toys	Permanently banned in EU; Potentially vulnerable population exposed; DEHP not currently used in toys in the US because of consumer relations; concern with imported products
Sheet/Film (e.g. food packaging)	FDA limits use of DEHP in packaging that touches food
Vinyl Shower Curtain	Not recommended for study because other applications with similar manufacturing process will be evaluated
Vinyl Wall Covering	High consumer exposure potential; large usage; ubiquitous
Car Undercoating	Alternatives available
Footwear	Alternatives available; further research to determine manufacturing in MA and US and potential consumer exposure.
Upholstery	High consumer exposure potential; large usage; ubiquitous
Medical Devices	
Plastic sheet materials (e.g. bags)	High usage; potentially vulnerable population exposed; many alternatives possible; Serious health issue; High concern to many stakeholders
Tubing (e.g. IV tubing)	High usage; potentially vulnerable population exposed; many alternatives possible; serious health issue; High concern to many stakeholders
Industrial/Commercial Uses	
Resilient flooring (also residential use)	Used in MA; high occupational exposure potential; alternatives available on the market
Roofing	Most roofers do not want or use products containing DEHP; alternatives available (stakeholder discussion 10/21)
Aluminum Foil Coating/ Laminating	Alternatives available
Paper Coating	Alternatives available
Extrudable PVC Molds/Profiles	Used in MA; 1% of total DEHP use; not identified as priority
Electronic Component Parts	Used in MA; less than 1% of total DEHP use; not identified as priority
Wire/Cable Coating Compounds	Used in MA; DEHP has been greatly reduced in MA due to use of alternative plasticizers

Table 7.2 B: DEHP Uses and Stakeholder Discussion

Uses/Applications	Stakeholder Discussion
Others: Lighting Ballasts and Electric Capacitors; Vacuum Pump Oil; Perfumes/Cosmetics; Pesticides; Printing Inks (e.g. lithographic); Paints and lacquers; Adhesives and Coatings; Ceramics	Very small amount of DEHP used in each of these products – not identified by stakeholders as applications of concern.

The priority uses of DEHP were selected based on predetermined criteria (refer to Appendix A) including:

- Quantity of DEHP in products and manufacturing in Massachusetts;
- Potential environmental and occupational exposure; and
- Availability of viable alternatives.

According to the criteria, the major DEHP uses that warranted further research in our alternatives assessment included:

Table 7.2 C: DEHP Preliminary List of Priority Uses

Use	Criteria Applied to Determine as Priority
Medical Sheet/Bag Devices in Neonatal Care	Potential public exposure; Many device manufacturers in Massachusetts; Many alternatives available
Medical Tubing Devices in Neonatal Care	Potential public exposure; Many device manufacturers in Massachusetts; Many alternatives available
Resilient Flooring	Largest DEHP manufacturer in Massachusetts; Potential occupational and public exposure; Many alternatives available
Footwear	Potential occupational and public exposure; Many alternatives available
Vinyl Wall Coverings	Potential occupational and public exposure; Many alternatives available

The Institute originally identified footwear as a priority industry for analyzing alternatives to DEHP. However, after further investigating DEHP use among Massachusetts footwear manufacturers, the Institute did not find any firms using DEHP in footwear. The one Massachusetts firm that manufactures footwear in the Commonwealth, New Balance, was contacted to discuss its use of DEHP. According to New Balance representatives, they phased DEHP out of their products several years ago. Several other footwear companies, including Timberland, Nike, and Adidas, have eliminated DEHP from products. Although there is likely some footwear imported into the Commonwealth containing DEHP, the Institute decided to focus its alternative analysis resources on vinyl wall coverings as the more pertinent consumer product use of DEHP.

This list of priority uses does not include two products that are of particular interest to certain stakeholders – toys and wire and cable coating compounds. Toys were not included because further research showed that DEHP has been eliminated from toys manufactured in the US in almost all applications. One of our stakeholders commented, "The global market is moving away from phthalates in toys." In addition, our conversations with toy manufacturers and their suppliers of plasticizers indicate that the US market has voluntarily moved away from the use of DEHP in response to the 1999 EU temporary ban on phthalates that was made permanent in 2004 (EU Marketing and Use Directive 76/769/EEC as amended) for certain phthalates present at greater than 0.1% for all toys and childcare articles. The Toy Manufactures of America (TMA) have stated that most manufactures of pacifier and toys have discontinued the use of the DEHP and DINP in their products (Hileman 2005).

The TMA set DEHP standards to less than 3% in pacifiers and teethers. This was done as part of an agreement with the U.S. Consumer Product Safety Commission (CSPC) in 1986. The CPSC stated that the projected cancer risk associated with exposure to DEHP has declined greatly after the phase of out of the chemical in pacifiers. However there is currently no federal US regulation restricting the use of DEHP in toys. Stakeholders expressed concern about imported products still containing DEHP. However, overall stakeholders saw little benefit from including this application in the alternatives assessment.

Wire and cable coating compounds were also not included because further research with local companies as well as the stakeholders indicates that DEHP use in wire and cable has already been greatly reduced in Massachusetts. This reduction is largely due to the availability of a number of viable alternatives The alternatives are also being simultaneously assessed by an EPA sponsored Design for the Environment project, which is performing a life cycle assessment of alternative constructions for three wire and cable applications[18].

Further research on the major DEHP uses was completed, presented and discussed at the third meeting with stakeholders. Additional feedback from the stakeholders was requested in order to identify the applications of DEHP to be examined for alternative applications. The final list of priority uses selected for further study is:

- Resilient Flooring
- Medical Devices (including sheet and tubing uses, with a specific focus on the use of these devices in neonatal care)
- Vinyl Wall Coverings

7.3 DEHP Alternatives Identification and Prioritization

For the priority uses that have been selected, DEHP is used for its functionality as a plasticizer. Therefore, when considering alternatives to DEHP there are two distinct strategies that can be employed:

1. Substitute an alternative plasticizer; or
2. Substitute an alternative material or technology that does not require the use of a plasticizer.

These alternatives are referred to herein as plasticizer and material alternatives. Technological alternatives will be addressed on a use-specific basis as appropriate. As described within the methodology for this project (Appendix A), factors leading to determining priority alternatives include:

- Performance criteria;
- Availability of alternatives;
- Manufacturing location;
- Environmental, health and safety considerations;
- Cost;

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[18] Go to http://www.epa.gov/dfe/pubs/projects/wire-cable/index.htm for information on this program.

- Global market effects; and
- Other issues pertinent to that particular use.

These factors are not necessarily weighted the same for each use. The Institute determined which factors present the most significant role in determining preferred alternative plasticizers and materials. For material alternatives the Institute has also taken into account significant life cycle considerations when determining priority alternatives. Technological alternatives often require a more in depth life cycle assessment to evaluate how the alternative compares to the original technology. Therefore, unless existing life cycle assessments are available for technological alternatives (*e.g.,* painting rather than covering walls with a material), the Institute did not focus its efforts on these alternatives to uses of DEHP.

7.3.1 Alternatives Associated with Resilient Flooring

Available Alternatives

This study focuses on alternatives to DEHP/PVC residential resilient flooring. Resilient flooring is defined as tile and sheet materials which have the ability to return to their original form after compacting (Vinyl by Design (VBD) 2006). When considering alternatives to DEHP in resilient flooring the comparison must include different materials as well as different plasticizers. Based on our evaluation, no specific technological alternatives are associated with this use.

Plasticizer alternatives in resilient flooring that were identified from stakeholder conversations, discussions with industry experts and literature research include:

- DINP (di isononyl phthalate)
- DIDP (di isodecyl phthalate)
- DEHT (di(2-ethylhexyl)terephthalate)
- BBP (butyl benzyl phthalate)
- DGD (dipropylene glycol dibenzoate)
- DEGDB (diethylene glycol dibenzoate)
- DEHA (di(ethylhexyl) adipate)
- DEHPA (di(2-ethylhexyl) phosphate)
- DHP (di isohexyl phthalate)
- BOP (butyl, 2-ethylhexyl phthalate)
- DBP (dibutyl phthalate)
- TCP (tricresyl phosphate)
- TEGDB (triethylene glycol dibenzoate)
- ATBC (o-acetyl tributyl citrate)
- DBS (dibutyl sebacate)
- DIHP (di (isoheptyl)phthalate)
- 97A (hexanadedioic acid, di-C7-9-branched and linear alkyl esters)
- TXIB (butane ester 2,2,4-trimethyl 1,3-pentanediol di isobutyrate

Material alternatives were also considered as replacements for the DEHP/PVC blend used as resilient flooring in residential, industrial and commercial settings. The following list, developed based on literature and market research and discussions with industry experts, presents the material alternatives that were considered at this stage of the process:

- Bamboo
- Natural Linoleum
- Cork
- Polyolefin
- Polyethylene/limestone blend
- Rubber
- Concrete
- Terrazo
- Concrete and recycled glass blend
- Wood

Alternatives Screened Out for Resilient Flooring

The methodology for screening potential alternatives presented in Section 2 (and is presented in more detail in Appendix A) was applied to the plasticizer alternatives. Table C5 (in Appendix C) presents the information used to determine if any of the plasticizer alternatives had to be screened out based on being carcinogenic, on the list of more hazardous substances or a PBT. It is important to note on Table C5 that in several instances no data were available for one of the criteria for a specific alternative. In this case, the chemical was not eliminated from further study.

Based on this analysis, the following chemicals were screened out for further analysis:

- DIHP (di (isoheptyl) phthalate) - Failed due to sediment persistence and aquatic toxicity
- 97A (hexanadedioic acid, di-C7-9-branched and linear alkyl esters) – Failed due to sediment persistence and aquatic toxicity
- TXIB (butane ester 2,2,4-trimethyl 1,3-pentanediol di isobutyrate) – Failed due to sediment persistence and aquatic toxicity (also exhibits high bioaccumulation, though it does not exceed the screening level)

Several material alternatives were eliminated from further evaluation because they did not meet the resiliency criterion (*i.e.,* able to return to their original form after compacting) associated with this specific use category. Those materials include:

- Concrete
- Terrazo
- Concrete and recycled glass blend
- Wood
- Bamboo

Materials were not screened out from further evaluation because of other performance, environmental and human health, or economic considerations.

Priority Alternatives for Resilient Flooring

Based on our initial review of available alternatives it was apparent that there were a large number and variety of potential plasticizer alternatives available for resilient flooring. Therefore, in order to arrive at a manageable number of alternatives to assess fully, the Institute conducted a tiered approach to determining the priority alternatives.

Plasticizer Alternatives for Resilient Flooring

As part of the initial screening effort to determine alternatives to eliminate, several plasticizer alternatives were identified as having persistence, bioaccumulative or toxic values that exceeded the screening criteria (indicated as red on Table C5, Appendix C), with one of the other PBT criteria approaching a level of concern (indicated as orange on Table C5, Appendix C). Hence they were not screened out as PBTs, but have been flagged as being of concern because they approach the associated PBT screening levels.

These “P, B or T” alternatives include:

- DHP (di isohexyl phthalate)
- BOP (butyl, 2-ethylhexyl phthalate)
- DBP (dibutyl phthalate)

- BBP (butylbenzyl phthalate)
- TCP (tricresyl phosphate)
- DEGDB (diethylene glycol dibenzoate)
- TEGDB (triethylene glycol dibenzoate)
- ATBC (o-acetyl tributyl citrate)
- DBS (dibutyl sebacate)

Because there are numerous plasticizer alternatives available for this use that did not approach levels of concern, none of these alternatives were evaluated further.

Institute staff met with a resilient flooring manufacturer in Massachusetts to tour their production facility and discuss the manufacturing process and the use of DEHP in its products. The manufacturer's representative did indicate that alternative phthalates would potentially be appropriate alternatives to DEHP from a technical standpoint, but added that this would mean certain financial impacts associated with raw material costs and required process modifications. He further indicated that in today's very competitive market, economic factors become primary operating considerations in this industry sector when choosing materials.

Several parameters were evaluated when determining which alternative plasticizers would be prioritized for further assessment. Specific performance considerations included the substance's compatibility with PVC. According to industry experts, the volatility of the plasticizer should not be higher than that of DEHP to assure similar processability. Adoption of alternative plasticizers that approach the technical and economic profile of DEHP/PVC would likely be more attractive to industry for adoption.

According to plasticizer and flooring manufacturers, plasticizer cost is the most important consideration when designing and marketing a product. The flooring market is so competitive today that increasing the cost of a product by a few cents could determine whether a product sells.

Table 7.3.1 A summarizes the considerations that the Institute used in determining if a plasticizer alternative would be eliminated from further evaluation.

Table 7.3.1 A: Considerations for Resilient Flooring Alternative Plasticizers

Environmental	Processability	Cost
Plasticizer alternative should not exceed any levels of concern for environmental screening criteria	Plasticizer alternative should not be significantly more difficult to process than DEHP	Plasticizer alternative should be no more than 10% greater than DEHP on a processed per pound basis

Table 7.3.1 B summarizes the cost, performance and environmental prioritization considerations for plasticizers that were factored into determining the alternatives to assess. Particular attention was paid to an alternative's ability to approach the technical and economic profile of DEHP.

Based on the considerations evaluated on Table 7.3.1B, the following alternative plasticizers appear to be suitable for further study for resilient flooring: DEHT, DINP, DGD, and DEHA.

Table 7.3.1 B: Resilient Flooring Plasticizer Prioritization Summary

Plasticizer	Performance and Cost Considerations									Environmental Considerations						Comments
	Processability				Physical Properties		Cost			Persistence				Bio-accum-ulation	Aquatic Toxicity	
	Vapor Pressure (mm Hg)	PVC Com-patibility	Com-pounding	Calender-ing	Emissions	Tensile Elongation	Raw material ($/lb)	Subst. Factor (phr)	Adj. Cost	Water	Soil	Sed.	Air	BCF	Chronic Fish ChV (mg/L)	
DEHP Di-2-ethylhexyl phthalate	**1.4 x 10^{-6}**	**Ref.**	**Ref.**	**Ref.**	**Ref.**	**Ref. MW 390**	**$0.70**	**1**	**$0.70**	**15**	**30**	**140**	**0.75**	**310** **580**	**No effect at 0.0025 mg/1**	
DINP Di isononyl phthalate	5.4 x10^{-7}	Good	Similar to DEHP	Higher process temp >2 C°	Similar to DEHP	higher MW 418	$0.73	1.06	$0.77	15	30	**140**	0.67	3.2	**>0.14** mg/L @ 96 hr	
DIDP Di isodecyl phthalate	3.7 x 10^{-7}	Good	Similar to DEHP	Higher process temp >2 C°	Similar to DEHP	Higher MW 446	$0.77	1.1	$0.85	38	**75**	**340**	0.62	3.2	Not Est.	Exceeds two **P** criteria; Cost 10% greater than DEHP
DEHT Di 2-ethylhexyl terephthalate	2.14 x 10^{-5}	Good			Similar to DEHP	Same MW 390	$0.72	1.03	$0.74	15	30	**140**	0.75	25	> **0.015** mg/L	
BBP Butyl benzyl phthalate	7.7 x 10^{-6}	Good			Similar to DEHP	Lower MW 312	$0.70	0.94	$0.66	15	30	**140**	**1.5**	880	**0.081**	Exceeds **P** and **T** criteria
DGD Dipropylene glycol dibenzoate	5.2 x 10^{-6}	Good	Easier than DEHP	No issues identified	Similar to DEHP	Lower MW 342	$0.73	0.98	$0.72	15	30	**140**	0.46	190	**0.55**	
DEHA Di 2-ethylhexyl adipate	8.5 x10^{-7}	Fair	More difficult than DEHP	Similar to DEHP	Somewhat lower volatility	Similar to DEHP MW 371	$0.74	0.94	$0.70	8.7	17	**78**	0.62	61	>100 mg/L at 96 hr.	

Table 7.3.1 B: Resilient Flooring Plasticizer Prioritization Summary

Plasticizer										**Environmental Considerations**						**Comments**
					Physical Properties		**Cost**			**Persistence**				**Bio-accum-ulation**	**Aquatic Toxicity**	
		PVC Com-patibility	Com-pounding	Calender-ing	Emissions	Tensile Elongation	Raw material ($/lb)	Subst. Factor (phr)	Adj. Cost	Water	Soil	Sed.	Air	BCF	Chronic Fish ChV (mg/L)	
DEHP Di-2-ethylhexyl phthalate		**Ref.**	**Ref.**	**Ref.**	**Ref.**	**Ref.** **MW 390**	**$0.70**	**1**	**$0.70**	**15**	**30**	**140**	**0.75**	**310** **580**	**No effect at 0.0025 mg/l**	
DEHPA Di 2-ethylhexyl phosphate	4.7 x 10^{-7}	Good	Difficult	Similar to DEHP	Similar to DEHP	MW 322	$2-3	1	$2-$3	15	30	**140**	0.25	49	Not Est.	Signifi-cantly more expensive

Notes: *Refer to Appendix C for specific references for the environmental considerations*
Cost data obtained from industry sources, and reflect current US prices in March 2006
Processability data obtained from various industry sources, including trade organization data, individual chemical technical data sheets and MSDS
Comments based on review of presented data and stated prioritization criteria

Alternative Materials for Resilient Flooring

Considerations for alternative resilient flooring materials are outlined in Table 7.3.1 C. Material alternatives that do not satisfy any of these considerations are deemed less feasible as alternatives to DEHP/PVC flooring. As noted, the Institute included maintenance and durability as key considerations for comparing material alternatives to DEHP/PVC in addition to cost and performance considerations.

Table 7.3.1 C: Considerations for Resilient Flooring Material Alternatives

Performance	**Maintenance /Durability**	**Cost**	**Environmental**
Avoid the following: • Limited stock available • Lifetime less than 1 year	Materials should not require daily polishing and/or waxing	Cost should not be significantly higher than DEHP/PVC (*i.e.,* >$15/sf)	Materials should not be petrochemical based, preferentially from renewable resources, do not require the use of toxic chemicals in their manufacture or installation, and do not off-gas VOCs.

Table 7.3.1 D summarizes the cost, performance and environmental prioritization considerations for materials that were factored into determining the alternatives to assess. Particular attention was paid to an alternative's ability to approach the technical and economic profile of DEHP/PVC.

Based on the information presented in Table 7.3.1D, natural linoleum, cork and polyolefin all came through as priority alternatives for DEHP/PVC.

Both the polyethylene/limestone blend and rubber are feasible alternatives to DEHP/PVC flooring based on the majority of the factors considered. However the Institute identified limitations for each of these materials that made them less favorable alternatives compared to the other materials identified and they were therefore not considered further in this study. Specifically, although the polyethylene/limestone blend looked like a very viable alternative to DEHP/PVC from a performance and cost standpoint, it is not manufactured or readily available in the US at this time. The one distributor identified was contacted and is apparently not actively marketing this product. While rubbers have clear applicability in certain industrial and high traffic commercial applications (*e.g.,* in health care settings) at consistent cost and performance to DEHP/PVC, the limited nature of color alternatives makes rubber a less attractive alternative for light commercial (*e.g.,* office) or residential applications. It should be noted however that the range of colors and patterns available in synthetic rubber floorings is increasing.

Table 7.3.1 D: Resilient Flooring Material Prioritization Summary

Material	Performance			Availability (No. of suppliers/mfgr)	Cost (purchase & install.) $/sf	Environmental		Comments
	Maintenance / Durability	Lifespan (years)	Colors/ Patterns			Hazards	Benefits	
DEHP/PVC	Clean with water and ammonia when needed. Many require routine stripping and wax reapplication.	25+	Many	Many	$3-8	Ref.	Ref.	
Natural Linoleum	Dust mop, vacuum or sweep with a broom to remove grit and dust from the surface	40+	Many patterns and colors	Many	$3-6	Outgases linseed oil VOCs	Rapidly renewable, decomposes in dump, may be compostable	
Cork	Sweep or vacuum floor frequently. Wet maintenance is entirely forbidden. Recoat with polyurethane 4-8 yrs or when floor starts to show wear	80+	Limited solid colors	Many	$6 - $11.50	Some manufacturers use urea formaldehyde binders (*see section on formaldehyde*)	Rapidly renewable, biodegradable at end of useful life	
Polyolefin (Stratica)	Sweep or vacuum floor frequently; mop with water when necessary		Wood and stone prints	Many	$6.50/sf	Petrochemical based	Low VOC, solvent free adhesive, limited recycling	
Polyethylene / Limestone (LifeLine)	Moist or wet-cleaning method with mildly alkaline cleaner should be used	30-50	Many colors stone prints	Despite printed literature, does not appear to be available in the US	$5-$6	Installed with a regular acrylic based adhesive	Recycled during production, disposed of by burning and used as an energy waste since contains no PVC	Not currently available in the US
Rubber	Sweep or vacuum to remove loose dirt, spot clean and use damp mop		Limited colors and prints	Many	$3-10	Some outgas of VOCs – varies between differing products	Recyclable but no infrastructure to take back	Limited colors and prints; more of a niche product for high traffic industrial & commercial installations.

Alternatives to be Assessed for Resilient Flooring

Table 7.3.1 E presents the list of alternatives that were assessed more fully for resilient flooring uses:

Table 7.3.1 E: Priority Alternatives for Resilient Flooring

Priority Alternative Plasticizer	Priority Alternative Material
DEHT	Natural linoleum
DINP	Cork
DGD	Polyolefin
DEHA	

7.3.2 Alternatives Associated with Medical Devices for Neonatal Care

Available Alternatives

Information on available alternatives was obtained from technical experts in the manufacturing and health care industries, public health organizations, and academia and from literature searches. Because the focus was on medical devices for neonatal care, stakeholders pointed out the importance of a careful evaluation of alternatives, both to ensure reliable performance, and to minimize the risk to a sensitive population. One Massachusetts stakeholder is currently working on manufacturing non-DEHP devices, and specifically requested that the Institute assess DINCH, which is an alternative plasticizer that has received limited review by other sources. To obtain additional insight into the toxicology of DEHP and some of the alternatives, a meeting was held in Lowell with experts from industry, health care and academia.

There are two distinct categories of medical devices used for infants in neonatal intensive care facilities that were the focus of this study: bag/sheet devices containing plasticizers, and tubing containing plasticizers. As with the resilient flooring use, alternatives that are investigated for these applications include alternative plasticizers and alternative materials. For this use, process changes were not evaluated. Specifically, the option of foregoing medical procedures in order to avoid exposure to medical devices that contain DEHP is not an acceptable alternative.

Much work has been done to evaluate the material properties and processing of alternatives to DEHP plasticizers and PVC (one of the primary materials used) in the healthcare industry. The Danish Environmental Protection Agency has conducted significant research into alternatives for healthcare applications (Danish Environmental Protection Agency (DEPA) 2003), including conducting research to confirm certain technical parameters of a variety of alternative plasticizers in PVC. Health Care Without Harm (HCWH) is a leading advocacy and policy research organization concerned with identifying and promoting the use of safer materials in the healthcare environment. It has reported on alternatives, focusing primarily on alternative materials to PVC, in several reports, including "Neonatal Exposure to DEHP and Opportunities for Prevention" (Rossi 2002). While this report emphasizes alternatives to PVC, it includes detailed research and discussion on the use of DEHP in PVC-based products. Concurrently, many companies that manufacture medical devices have been developing products made from alternative materials. These represent some of the major sources of information the Institute used when identifying and prioritizing alternatives for medical devices used for neonatal applications.

Plasticizer Alternatives

The Danish EPA was interested in evaluating the performance and environmental issues associated with representative plasticizer alternatives. The suite of alternative plasticizers identified as warranting further investigation by this Danish agency includes:

- DINP
- DEHA
- DEHS, di(2-ethylhexyl) sebacate
- TOTM, triethylhexyl trimellitate
- ATBC, acetyltributyl citrate
- Benzoates (potentially DGD)
- Polymeric adipates
- Ethylene-acrylate-carbon monoxide terpolymer (Elvaloy®)

The HCWH evaluations were more focused on the use of alternative materials; however, they also assessed the availability, performance and EHS implications of various alternative plasticizers used in the US. Two alternative plasticizers they identified as being used or available in the US that were not identified as warranting further evaluation by the Danish EPA were:

- DBS (di butyl sebacate)
- BTHC (butyryl trihexyl citrate)

Finally, one of the study stakeholders, a manufacturer of medical devices in Massachusetts, specifically requested that the Institute include di (isononyl) cyclohexane-1,2-dicarboxylate (DINCH) in its alternatives assessment for medical device applications as it represents an emerging alternative plasticizer that they are considering.

Materials Alternatives

The options available for alternative materials in medical device applications are more limited. Again, the Institute relied on existing and timely research conducted by other organizations, as well as research into alternative materials hospitals and medical device manufacturers are currently using, to determine potentially suitable alternative materials. Five materials were identified:

- Ethyl Vinyl Aacetate
- Polyolefins (Polyethylene and Polypropylene)
- Thermoplastic Polyurethane
- Glass
- Silicone

Priority Alternatives for Medical Devices for Neonatal Applications

When determining which plasticizer and material alternatives to prioritize for further study, the Institute relied heavily on existing and timely studies conducted by other organizations (primarily the Danish EPA and HCWH), and the feedback received from our stakeholders.

Plasticizer Alternatives

The Institute was interested in focusing on a representative set of alternatives that approaches the cost and performance characteristics of DEHP while not approaching levels of concern from an EH&S standpoint. Each of the alternatives listed above has been identified by the Danish EPA, HCWH and/or stakeholders because they are feasible alternatives from a performance basis. The Institute focused its research at this stage on EHS and cost considerations, and on choosing representative plasticizers when determining the final list of priority alternative plasticizers to assess for medical devices.

Of the plasticizer alternatives listed above, there is a wide range of plasticizer types represented, including phthalates (DINP), adipates (DEHA and polymeric adipates), sebacates (DEHS and DBS), trimellitates (TOTM), citrates (ATBC and BTHC), benzoates (DGD), a terpolymer (Elvaloy®) and carboxylates (DINCH).

A review of PBT data (see Table C5 in Appendix C) indicates that the following plasticizers exhibit chronic aquatic toxicity and sediment persistence levels that approach or exceed levels of concern: ATBC, DGD and DBS. Therefore, these alternatives were not assessed further.

From a cost standpoint, many of the plasticizer alternatives are in a cost range that would likely be acceptable for the medical device industry. However other alternative plasticizers exhibit costs that may not be acceptable in this industry.

Alternative plasticizers with higher costs (based on creating a functional plastic with a hardness rating of 70 Shore A[19]) include:

- DINCH (cost ~$0.91 /lb – March 2006 industry data)
- TOTM (cost $1.11 /lb – March 2006 industry data)
- BTHC (cost ~$1.12 /lb – March 2006 industry data)
- Elvaloy® (cost ~$4.10 /lb – based on Danish EPA information)
- DEHS (estimated cost ~$4.50 /lb – based on Danish EPA information)
- Polymeric adipate (cost ~$6.00 /lb – based on Danish EPA information)

Based on these figures, Elvaloy®, DEHS and polymeric adipate appear to be in a range that is significantly greater than the estimated cost of DEHP (~$0.70/lb) and therefore will not be assessed further.

Material Alternatives

Based on our review of the above-mentioned studies, the Institute determined that all five of the alternative materials to DEHP/PVC (*i.e.,* ethyl vinyl acetate, polyethylene, polyurethane, glass, and silicone) warranted further assessment.

Alternatives to be Assessed for Medical Devices for Neonatal Applications

Table 7.3.2 A summarizes the final list of high priority alternatives for full assessment for medical device applications.

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[19] 70 Shore A is a standard hardness rating for flexible plastics, and allows for a functionally equivalent cost comparison

Table 7.3.2 A: Final Alternatives for Medical Device Neonatal Applications

Priority Alternative Plasticizer	Priority Alternative Material
TOTM	Ethyl vinyl acetate
DEHA	Polyolefins
BTHC	Glass
DINP	Silicone
DINCH	Thermoplastic Polyurethane

7.3.3 Alternatives Associated with Wall Coverings

This study focuses on alternatives to DEHP/PVC, or vinyl, residential wall covering. When considering alternatives to DEHP in vinyl wall coverings the comparison must include different materials as well as different plasticizers. Process alternatives such as painting or paneling are alternatives that are also available for vinyl wall coverings.

Available Alternatives for Wall Coverings

Plasticizer alternatives for vinyl wall coverings that were identified from stakeholder conversations, discussions with industry experts and literature research include:

- DINP
- DIDP
- TOTM
- DEHA
- DEHPA
- TOP (tri (2-ethylhexyl) phosphate)

Material alternatives for DEHP/PVC blend used in wall coverings, developed based on literature and market research and discussions with industry experts, include:

- Glass Woven Textiles
- Wood Fiber/Polyester
- Polyethylene
- Cellulose/Polyester
- Polyester
- Biofibers
- Polyolefins
- Recycled Paper
- Wool/Ramie

Finally, there are viable process alternatives to vinyl wall coverings, including painted wall surfaces or different wall materials (such as pine paneling). They differ significantly from wall coverings in terms of aesthetics, but can be functionally equivalent. These technological alternatives have many issues associated with them throughout their life cycle. Because a full life cycle assessment is beyond the scope of this study, and because many plasticizer and material alternatives are available for assessment, the Institute is not evaluating technological alternatives in the full assessment. However, it is important to note that painting and other wall materials are indeed viable alternative to the use of vinyl wall coverings.

Alternatives Screened Out

None of the plasticizer or materials alternatives identified above were screened out due to EH&S issues. However, the plasticizers that were screened out as discussed in the resilient flooring section (Section 7.3.1) were also not considered for this application.

Priority Alternatives for Wall Coverings

Based on our initial review of available alternatives it is apparent that there is a large number and variety of potential plasticizer alternatives available for wall coverings. Therefore, in order to arrive at a manageable number of alternatives to assess fully, the Institute conducted a tiered approach to determining the priority alternatives.

Plasticizer Alternatives for Wall Coverings

Several criteria were considered when determining which alternative plasticizers would be prioritized for further assessment. Plasticizers should exhibit equal or improved characteristics from an environmental and human health standpoint than DEHP. Adoption of alternative plasticizers that approach the technical and economic profile of DEHP/PVC will be more attractive to industry for adoption. Substances that are incompatible will not plasticize PVC properly. In addition, the volatility of the plasticizer should not be higher than that of DEHP in order to assure similar processability. According to plasticizer and wall covering manufacturers, plasticizer cost is the most important consideration when designing and marketing a product.

Table 7.3.3 A summarizes the considerations that the Institute used in determining if a plasticizer alternative would be eliminated from further evaluation.

Table 7.3.3 A: Considerations for Wall Covering Plasticizer Alternatives

Processability	Cost	Environmental
Plasticizer alternative should not be significantly more difficult to process than DEHP	Plasticizer alternative should not be more than 10% greater than DEHP on a processed per pound basis	Plasticizer alternative should not exceed any levels of concern for environmental screening criteria

The plasticizer alternatives to DEHP vinyl wall coverings are listed in Table 7.3.3 B. These DEHP plasticizer alternatives include other phthalates, as well as trimellitates, adipates and phosphates. Each of these plasticizers is known to be an available alternative to DEHP in vinyl wall covering.

Table 7.3.3 B: Wall Covering Plasticizer Prioritization Summary

Plasticizer	Performance and Cost Considerations									Environmental Considerations						Comments
	Processability				Physical Properties		Cost			Persistence				Bio-accum-ulation	Aquatic Toxicity	
	Vapor Pressure (mm Hg)	PVC Com-patibility	Com-pounding	Calender-ing	Emissions	Tensile Elongation	Raw material ($/lb)	Subst. Factor (phr)	Adj. Cost	Water	Soil	Sed.	Air	BCF	Chronic Fish ChV (mg/L)	
DEHP Di-2-ethylhexyl phthalate	**1.4 x 10^{-6}**	**Ref.**	**Ref.**	**Ref.**	**Ref.**	**Ref. MW 390**	**$0.70**	**1**	**$0.70**	**15**	**30**	**140**	**0.75**	**310**	**No effect @ 0.0025 mg/L**	
DINP Di isononyl phthalate	5.4 x10^{-7}	Good	Similar to DEHP	Higher process temp >2 C°	Similar to DEHP	higher MW 418	$0.73	1.06	$0.77	15	30	**140**	0.67	3.2	>0.14 mg/L at 96 hr	
DIDP Di isodecyl phthalate	3.7 x 10^{-7}	Good	Similar to DEHP	Higher process temp >2 C°	Similar to DEHP	Higher MW 446	$0.77	1.1	$0.85	38	**75**	**340**	0.62	3.2	Not Est.	Exceeds two **P** criteria; Cost 10% greater than DEHP
TOTM tri-2-ethylhexyl trimellitate	4.5 x 10^{-8}	Good	Slightly harder than DEHP	Similar to DEHP	Lower than DEHP	Higher MW 546	$0.95	1.17	$1.11	8.7	17	**78**	0.5	3.2	>100 mg/L at 96 hr.	Sediment **P** above level of no concern; Significantly lower volatility; Cost significantly higher than DEHP
DEHA Di 2-ethylhexyl adipate	8.5 x10^{-7}	Fair	More difficult than DEHP	Similar to DEHP	Similar to DEHP	Similar to DEHP MW 371	$0.74	0.94	$0.70	8.7	17	**78**	0.62	61	>100 mg/L at 96 hr.	
DEHPA Di 2-ethylhexyl phosphate	4.7x 10^{-7}	Good	Difficult		Similar to DEHP	MW 322	$2-3	1	$2-$3	15	30	**140**	0.25	49	Not Est.	Significantly more expensive

Table 7.3.3 B: Wall Covering Plasticizer Prioritization Summary

Plasticizer	Performance and Cost Considerations									Environmental Considerations						Comments
	Processability				Physical Properties		Cost			Persistence				Bio-accumulation	Aquatic Toxicity	
	Vapor Pressure (mm Hg)	PVC Compatibility	Compounding	Calendering	Emissions	Tensile Elongation	Raw material ($/lb)	Subst. Factor (phr)	Adj. Cost	Water	Soil	Sed.	Air	BCF	Chronic Fish ChV (mg/L)	
DEHP Di-2-ethylhexyl phthalate	**1.4 x 10^{-6}**	**Ref.**	**Ref.**	**Ref.**	**Ref.**	**Ref.** **MW 390**	**$0.70**	**1**	**$0.70**	**15**	**30**	**140**	**0.75**	**310**	**No effect @ 0.0025 mg/L**	
TOP tri(2-ethylhexyl) phosphate	1.5 x 10^{-5}	Fair	Difficult	Unknown	Somewhat higher than DEHP	Higher than DEHP MW 434.7	$2.10	1	$2.10	8.7	17	**78**	0.16	3.2	Not Est.	Sediment **P** above level of no concern; Processing difficult and only fair compatibility with PVC; Cost significantly higher than DEHP

Notes: *Refer to Appendix C for specific references for the environmental considerations*
Cost data obtained from industry sources, and reflect current US prices in March 2006
Processability data obtained from various industry sources, including trade organization data, individual chemical technical data sheets and MSDS
Comments based on review of presented data and stated prioritization criteria

Based on the information presented in Table 7.3.3C, the following plasticizer alternatives were identified to be assessed further: DEHA and DINP.

Alternative Materials for Wall Coverings

For material alternatives the Institute included maintenance/durability considerations as a key consideration for selecting alternatives to DEHP/PVC in addition to cost and performance considerations. Table 7.3.3 C summarizes the undesirable attributes for wall covering material alternatives.

Table 7.3.3 C: Considerations for Wall Covering Material Alternatives

Performance	Maintenance /Durability	Cost	Environmental
Material should have a variety of colors and patterns available. The estimated life time usability should not be significantly shorter than for DEHP /PVCwall covering.	Material should not be easily stained or damaged. It should not be especially difficult to clean.	Materials should not be significantly higher than DEHP/PVC (>$25/yd)	Materials should not be petrochemical based, preferentially from renewable resources, do not require the use of toxic chemicals in their manufacture or installation, and do not off-gas VOCs.

The material alternatives to DEHP/PVC wall coverings are listed in Table 7.3.3 D. The table summarizes reasons why particular materials were eliminated from further study.

Table 7.3.3 D: Wall Covering Material Prioritization

Material	Performance		Cost (1) (purchase & installation) ($/yard)	Global Market Effect (e.g. restrictions)	Other	Environmental		Comments
	Maintenance / Durability	Lifespan (years)				Hazards	Benefits	
DEHP/PVC (Vinyl)	**Scrubbable and washable**	**25+**	**$3 -5 low end; $14- $22 high end**	**Some architects and designers are voluntarily moving away from DEHP/PVC products**		**Ref.**	**Ref.**	
Glass Woven Textiles	Clean with damp cloth, can be scrubbed if necessary. Can repaint up to 10 times to change appearance or cover scuffs.	20+	$13-$15		Used in Europe for over 60 years. Mold/mildew resistant		Made from sand (woven glass) and recycled glass. Can be covered with any latex or special finish paint.	
Wood Fiber/ Polyester	Scrubbable using soft bristle brushes only	1 year warranty	$13		Not recommended for high-moisture areas; Not scrubbable; Not good for high traffic areas		50% wood pulp and 50% spun-woven polyester fibers; No heavy metals or formaldehyde; Water soluble inks	
Polyethylene	Periodic vacuuming; Aggressively scrubbable	20+	$28-30 (material only)	Petrochemical product very durable; Low VOCs	Water repellant, stain resistant; Anti-bacterial, antifungal and non-toxic.		Contains no PVC, no Chlorine, is plasticizer free, heavy metal free and inherently flame retardant.	High cost
Cellulose/ Polyester	Scrubbable	10-15	$18-$22 (material only)	Product take-back program available. Duraprene uses recycled products	Can be used in all areas "similar to vinyl" except this product breathes reducing mold and mildew		Cellulose totally chlorine free. Does not emit any VOC's; Waterbased inks; Wood from sustainably managed forests	
Polyester	Occasional vacuuming recommended; Keeping the product clean is a problem		$30-$35				100% recycled and poly blends with natural fibers; Both post consumer and post industrial polyester used.	High cost, difficult maintenance

Table 7.3.3 D: Wall Covering Material Prioritization

Material	**Performance**		**Cost** (1) (purchase & installation) **($/yard)**	**Global Market Effect** (e.g. restrictions)	**Other**	**Environmental**		**Comments**
	Maintenance / Durability	Lifespan (years)				Hazards	Benefits	
DEHP/PVC (Vinyl)	**Scrubbable and washable**	**25+**	**$3 -5 low end; $14- $22 high end**	**Some architects and designers are voluntarily moving away from DEHP/PVC products**		**Ref.**	**Ref.**	
BioFibers	Light brushing and occasional vacuuming is recommended.						Contains post-consumer recycled material;, Releases minimal pollutants (including VOCs); Rapidly renewable Biodegradable	
Polyolefins	Will not absorb stains		$18-$22 (material only)			Teflon finish to enhance "cleanability" and ensure adhesives do not seep thru surface	100% Polyolefin and 85% polyolefin/ 15% polyester blend treated with Teflon finish.	
Recycled Paper	All stains should be treated ASAP with clean water. Harder stains can be treated with a mild detergent. Avoid rubbing. Occasional vacuuming	1 year warranty	$15.00 (> 200 yards) $16.50 (≤ 200 yards) plus installation		Installation by professional textile wall cover installer recommended (per web site)		Made from Japanese phonebooks (50-75% recycled books and the rest paper pulp).	Short life span, difficult maintenance
Wool/Ramie			$50-$67				Custom high end fabric which has low impact manufacturing.	Very high cost

Notes: (1) *Cost includes $7 to $10 per yard for installation*

Comments based on review of presented data and stated prioritization criteria

Alternatives to be Assessed for Wall Coverings

Our prioritization evaluation of alternatives resulted in the following list of alternatives that will be assessed more fully (Table 7.3.3 E):

Table 7.3.3 E: Final Alternatives for Wall Coverings

Priority Alternative Plasticizer	Priority Alternative Material
DEHA, di (2-ethylhexyl) adipate	Glass Woven Textiles
DINP, di(isononyl) phthalate	Cellulose/Polyester Blends
	Wood Fiber/Polyester Blends
	Biofibers
	Polyolefins

7.4 DEHP Alternatives Assessment

This section reviews the various priority plasticizer and material alternatives to DEHP identified using the criteria and methods described in Section 7.3. The following sections outline the assessment of these potentially viable alternatives. The alternatives assessment for each use is organized by plasticizer and material alternatives, with specific discussions of EH&S, technical and economic factors for each use within that overall heading. However, there are also common issues for plasticizers that apply to all the applications. These issues are discussed in a separate section, below.

Common Issues for DEHP Plasticizer Alternatives

Various plasticizer alternatives were identified through a literature review and discussions with industry manufacturers, processors, and end users. The Institute established desired criteria for cost, performance, environmental health and safety and cost for each alternative plasticizer that were used in assessing the feasible alternatives. Table 7.4 A summarizes these criteria.

Table 7.4 A: DEHP Plasticizer Alternative Assessment Criteria

Category	Assessment Criteria
Performance	The following performance criteria are important when substituting plasticizers in flooring and wall covering operations: • Lower plasticizer volatility, measured by plasticizer's vapor pressure, increases a product's expected lifetime. Ideally, the volatility of a substitute plasticizer should be equal to or lower than DEHP. • Compatibility measures how well a plasticizer is suited to PVC. Plasticizers with low compatibility are known to migrate out of plastic over the life of a product. • Molecular weight is a good indication of tensile elongation. Higher molecular weight plasticizers tend to result in longer product life • Compounding and calendaring processability compared to DEHP. These processes are most common when manufacturing flexible PVC. Alternatives should ideally process as well as or better than DEHP. The following additional performance criteria are important when substituting plasticizers in medical device applications: Sheet applications: Tensile strength, cold flexibility (because solutions must be cold-storable) and clarity are key considerations. Tubing applications: In addition to the considerations for sheet applications, elastic recovery is an essential consideration to assure that tubing does not kink during use. Solvent cementability to assure sound bonds between parts.
Financial	Cost data from industry sources in March 2006, based on a hardness rating of 70 Shore A. Cost estimates use plasticizer substitution factors to determine the relative amount of plasticizer, compared to DEHP, needed to obtain a particular level of hardness. For example, a factor of 1.1 indicates to achieve similar hardness; 1.1 times the amount of DEHP used is required.
Environmental Health and Safety	• Critical criteria were associated with the initial screen (*i.e.,* no PBT, Class 1 or 2 carcinogens or TURA SAB more hazardous chemicals). No chemicals that exceeded these criteria were put forward for further assessment. • If a plasticizer exhibits PBT values that approach levels of concern, as identified by the EPA in its PBT Profiler methodology, it will be considered less favorably in the assessment phase. • Additional parameters that are considered when assessing plasticizer alternatives have been identified based on the characteristics of DEHP and specific concerns relative to the likelihood of an effect occurring. These additional health criteria include: water solubility, octanol-water partition coefficient (a measure of hydrophobicity), organic carbon partition coefficient (sediment affinity indicator), lethal dose value (using the oral rat value as the benchmark), immediately dangerous to life and health (IDLH) value, permissible exposure limit, reference dose, carcinogen classification, toxicity (EU R-phrase or present on the California Proposition 65 list), and vapor pressure. For medical device applications particular attention needs to be paid to the ability of the plasticizer to migrate out of the polymer matrix and into the contained solution, thereby increasing the likelihood of exposure and associated health impact. Associated generation of metabolites of concern (based on associated environmental and human health effects) when the plasticizer enters the body must also be considered

Technical Issues Associated with Plasticizer Alternatives

As indicated in Table 7.4A, some of the technical issues associated with plasticizer alternatives are common regardless of the application for the plasticizer. Below is a discussion of those common technical issues.

PVC Compatibility

One of the most important factors determining the feasibility of a plasticizer as an alternative to DEHP is its overall compatibility with PVC. Plasticizers are assessed on their PVC compatibility based on their ability to create a stable compound (*i.e.,* create a single phase). An incompatible plasticizer will exude to the surface of the plastic making it more easily extracted by either volatilization into the air, or solubilization into the contact solution. In effect, this will result in a less flexible plastic than originally designed. In addition, the plasticizer needs to be compatible with any other additive that may be compounded into the plastic product. An indication of a poorly compatible plasticizer would be the loss of flexibility and/or a sticky or oily surface of the product.

To process well, plasticizers must be absorbed into the PVC resin particles during the blending process (DEPA 2003). Known as processability, PVC resin, plasticizer(s), stabilizers and lubricants should blend together readily in a compounding operation.

Migration or Permanence of Plasticizer

DEHP can migrate out of the PVC matrix because it is not permanently or covalently bound to the plastic molecule, therefore exposure to DEHP from the polymer matrix is a possibility. The mechanisms that control migration from a plastic, excluding the effects of plastic weathering, are surface-controlled losses (such as volatility and aqueous solubility) and diffusivity. Most plasticizers have extremely low water solubility and therefore their losses into aqueous environments are controlled by surface mechanisms rather than by being drawn out of the plastic (diffused). Volatile losses of plasticizer are influenced by vapor pressure, solvency strength for the polymer and oxidative degradation of the plastic. Plasticizers like DEHP are highly lipid soluble and therefore, when in the presence of oily or fatty solutions, their losses from the plastic are controlled by diffusivity.

Financial Factors Associated with Plasticizer Alternatives

Because of extreme price competition in the PVC flooring and wall covering industry, even slightly more expensive plasticizers find difficulty gaining widespread acceptance.

Depending on the application, the concentration of plasticizers in the polymer matrix can be up to 40% of the product by weight. In this case, and when dealing with low margin industries, the cost premiums associated with some of the alternatives to DEHP may be unacceptable from an industry standpoint. A mitigating factor here is that the plasticizers typically do not replace each other on a 1:1 basis. Some plasticizers are more efficient, and therefore less is required to achieve the same level of hardness of the plastic product. This "substitution factor" will be presented throughout the discussion to normalize the costs as much as possible.

Table 7.4B presents estimates of plasticizer costs based on data obtained from industry sources in March 2006, and includes estimated substitution factors, which allow for a normalized comparison of costs based on how they are used to create a comparably flexible product (70 Shore A). For instance, DINP, with a substitution factor of 1.06, requires more plasticizer and DEHA with a 0.94 substitution factor requires less plasticizer to achieve the same hardness as DEHP.

It is important to note also that some of the plasticizer alternatives are relatively new, and cost may decrease as production increases. This trend, however, is limited by the molecular composition of the plasticizers; compounds with more carbon chains and more complex chemistries will necessarily be more expensive than simpler plasticizer molecules.

Table 7.4 B: Plasticizer Cost Estimates

Plasticizer	**Cost Estimate ($/lb)**	**Substitution Factor** (SF)	**Normalized Cost** (raw cost x SF)
DEHP	*$0.70*	*1*	*$0.70*
DEHA	$0.73	0.94	$0.70
DGD	$0.73	0.98	$0.71
DEHT	$0.74	1.03	$0.76
DINP	$0.74	1.06	$0.77
DINCH	$0.91	unknown	$0.91
TOTM	$0.95	1.17	$1.11
BTHC[20]	$1.15	0.975	$1.12

Data from Industry Sources, March 2006

Environmental and Human Health Issues Associated with Plasticizer Alternatives

As discussed in Section 7.2, the health and environmental impacts associated with the use of DEHP as a plasticizer relate first to potential exposures in manufacturing, and second to potential exposures due to leaching out of the PVC matrix. Other plasticizers may also produce exposure to humans or the environment by leaching out. The environmental and human health impact assessment of the use of alternative plasticizers will begin by examining the inherent hazards of the substances, followed by a review of the likelihood of migration out of a product, and continue with a discussion of the potential impacts associated with a resulting exposure. Specific criteria that will be focused on in our assessment have been identified in Table 7.4A.

7.4.1 Alternatives Assessment for Resilient Flooring

DEHP/PVC or vinyl flooring has been one of the most popular flooring types found from kitchens and bathrooms to hospitals and schools. In general, there are two types of DEHP/PVC flooring: sheet flooring (typically 6' or 12' wide) and tile (typically 12"x12" or 9"x9").

Composition

Vinyl sheet is made with a felt or vinyl backing and can be either rotogravure (printed) or inlaid. In rotogravure vinyl, a printed image is sandwiched between the backing, a mid layer and a top wear layer (see Figure 7.4.1A). Inlaid vinyl uses tiny vinyl granules from the backing all the way to the wear surface making it highly durable but available in fewer patterns and colors. DEHP/PVC flooring can also be finished with a polyurethane layer which increases wear resistance. The backing may be made up of cellulose fibers, glass fiber, styrene butadiene latex, or acrylic latex, along with inorganic fillers such as limestone and talc. The backing adheres to the plastisol PVC layer. Inlaid sheet DEHP/PVC may have a felt backing.

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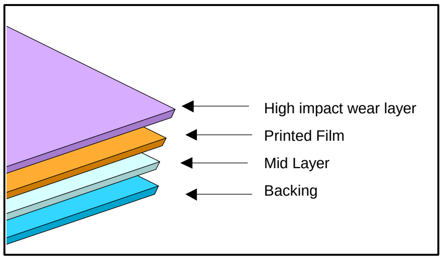
[20] Substitution Factor from manufacture's literature (http://www.morflex.com/pdf/bul101.pdf)

Figure 7.4.1 A: Common Rotogravure DEHP/PVC Sheet Construction



Vinyl composition tile (VCT) construction is very different from vinyl sheet. VCT contains a high proportion of inorganic filler (limestone) to increase its dimensional stability and reduce its elasticity.

Vinyl flooring varies widely in grade and quality with thinner grades priced lower. Figure 7.4.1 B shows several DEHP/PVC flooring samples.

Figure 7.4.1 B: Typical DEHP/PVC Tile Samples

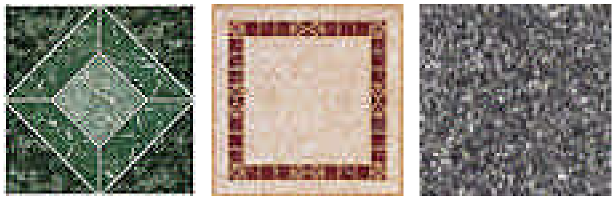


Table 7.4.1 A: Common Vinyl Flooring Compositions

DEHP/PVC Sheet Flooring Composition[21]		
Wt. %	Material	Origin/Precursor Materials
50%	PVC	Ethylene dichloride, vinyl chloride
30%	Plasticizer DEHP	Phthalic anhydride, 2-ethylhexyl alcohol
15%	Limestone	Mineral
~3%	Heat stab.	Barium zinc, calcium zinc[23]
~2%	Other ingredients	(e.g. titanium dioxide pigments, linseed oil)

DEHP/PVC VCT Flooring Composition[22]		
Wt. %	Material	Origin/Precursor Materials
12%	PVC	Ethylene dichloride, vinyl chloride
5%	Plasticizer DEHP	Phthalic anhydride, 2-ethylhexyl alcohol
80%	Limestone	Mineral
2%	Vinyl acetate	Ethylene, acetic acid
1%	Other ingredients	Stabilizers, etc.

Installation/Cleaning/Maintenance

Vinyl floors can be installed over wood, concrete or, in some cases, existing flooring. However, sub-flooring should be clean, smooth, of high quality and as flat as possible. Professional installation is often recommended to ensure long life. Daily sweeping or dust-mopping is recommended to

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[21] Source: (Potting and Blok 1995)

[22] Source: (Environmental Works Community Design Center (EWorks) 2002)

[23] According to the Resilient Floor Covering Institute, cadmium and lead based stabilizers are no longer used in vinyl flooring. Mixed metal stabilizers dominate the market in this application (see comments to USGBC LEED TSAC PVC Study Information Outreach Forum on stabilizers: http://pvc.buildinggreen.com/comments.php).

remove grit and dirt. Floors should be damp-mopped with a neutral detergent. Spills should be wiped up before they dry with a damp, clean white cloth. Many manufacturers recommend stripping and refinishing vinyl floors on a routine basis.

Resilient Flooring Financial Considerations

Typically, commercial vinyl composition floor tile has an installed cost of between $1.40 to $8.70 per square foot, depending on the thickness and pattern (this includes materials, equipment and labor). Commercial sheet vinyl has an approximate installed cost of $2.64 to $5.50 per square foot (VBD 2006). Higher quality vinyl flooring is thicker and is expected to last nominally from 25 to 30 years with proper cleaning and maintenance.

Environmental and Human Health Issues

The principal environmental and human health issues associated with DEHP/PVC flooring are outlined in Table 7.4.1 B. The PVC supply chain, including intermediates manufacturing and the various processing steps from crude oil and rock salt extraction through vinyl chloride monomer production, plays a major role in PVC impacts. Other impacts include energy use impacts from manufacturing and transport and a lack of end-of-life recycling and recovery options.

Table 7.4.1 B: General DEHP/PVC Alternative Material Assessment Criteria

Life Cycle Phase	Environment and Human Health Issues	Positive Aspects of DEHP/PVC
Raw Materials	• Extraction and refining of petroleum based feedstocks. • Ethylene feedstock is non-renewable • Few suppliers offer recycled content • A minority of DEHP/PVC is manufactured from chlorine made using the mercury cell process	• Some vinyl sheet manufacturers use up to 25% post-industrial recycled DEHP/PVC and reclaimed wood fibers in product.
Manufacture	• Human health impacts of PVC precursor chemicals • Energy use impacts: greenhouse gas, particulate, other • Potential worker exposure to DEHP during manufacture	• Post industrial vinyl scrap is recyclable
Installation	• Volatile organic compounds emitted from styrene butadiene floor adhesives	• Adhesives typically water-based, safer than older solvent-based types
Use and Maintenance	• DEHP exposure, though this is expected to be low due to the low vapor pressure • VOC emissions (rate depends on product type) • Most varieties require routine stripping and waxing, which may have associated VOC emissions	• Waxing and cleaning with mild detergent
End of Life	• Potential for chlorine derivative (dioxin and furan) emissions from improper combustion (accidental fire, backyard burning) • Chlorine derivatives may be found in fly ash of properly controlled incinerators • Not compostable • Lack of recycling infrastructure to recycle DEHP/PVC flooring	• Recyclable

Even though there is a great deal of information in the literature concerning life cycle impacts of using DEHP/PVC blends, there is no scientific consensus. This assessment attempts to lay out the key potential issues, allowing readers to draw their own conclusions.

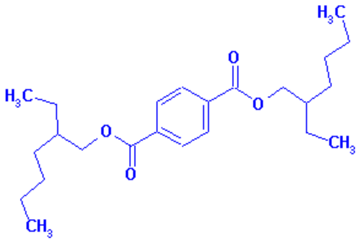
Specific Plasticizer Alternatives Assessed for Resilient Flooring

While DEHP is not the only plasticizer used in resilient flooring applications, it is the most commonly used plasticizer. Plasticizer alternatives that were prioritized for resilient flooring include DEHT, DINP, DGD and DEHA. These plasticizers represent a terephthalate, a phthalate, a dibenzoate and an adipate, as discussed in more detail below.

Di 2-Ethylhexyl Terephthalate (DEHT)

DEHT (di(2-ethylhexyl) terephthalate) is called a “phthalate like” plasticizer whose specific chemical structure is shown in Figure 7.4.1 C. DEHT has an isomeric structure of DEHP, which means that it has the same elements but has a different arrangement of the atoms. Although DEHT and DEHP are structurally similar, giving them almost identical physical-chemical properties, they have distinctly different toxicological properties. The performance of DEHT is similar to DEHP and its low cost often makes it a good alternative plasticizer. It is made by Eastman Chemical and known as Eastman 168 Plasticizer.

Figure 7.4.1 C: Chemical Structure of DEHT



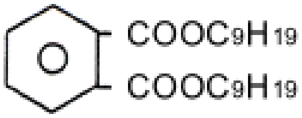
Rubber mat manufacturers have tried substituting DEHT and found that it does not work. There were issues because DEHT does not ‘take up’ fast enough and slows the process down (Biltrite 2005). DEHT used in rubber or PVC applications can, if not formulated properly, exude to the surface under warm and humid conditions when used in tightly coiled (Teknor Apex 2006). In addition, DEHT is slightly more volatile than DEHP, indicating that more may be required to make up for fugitive emissions during processing.

There are no workplace air exposure standards for DEHT. In a study conducted in 2002, the NOAEL for reproductive toxicity associated with exposure of rats to DEHT was considered to be 10,000 mg/kg bw/day. The NOAELs for parental toxicity and neonatal toxicity were considered to be 3,000 mg/kg bw/day (Faber et al. 2002). The persistence of DEHT in sediments and air is estimated as 140 days using the PBT Profiler methodology. Based on these few sources of information on impacts to human and environmental health due to exposure to DEHT, it appears that DEHT is of low concern.

Diisononyl Phthalate (DINP)

DINP is a mixture of phthalates with branched alkyl chains of varying length (C8, C9 and C10). The chemical structure of DINP is depicted in Figure 7.4.1 D. The plasticizing efficiency of DINP is somewhat lower than DEHP and therefore more plasticizer is required to gain the same softness. Because the molecular weight of DINP (418) is greater than DEHP (390), DINP has better high temperature performance and extraction resistance. Because DINP is less volatile than DEHP, processing with DINP leads to lower plasticizer losses during compounding and calendaring, reducing emissions and occupational exposure. According to one industry source, when compared with DEHP, DINP processing emits noticeably lower levels of plasticizer mist from process equipment.

Figure 7.4.1 D: Chemical Structure of DINP



DINP is a “drop in replacement” for DEHP. Because DINP has a lower volatility (5.4×10^{-7} mm Hg) than DEHP (1.4×10^{-6} mm Hg) the emissions from the operation using DINP may be lower. In one Massachusetts factory, line workers observed a clearer room (less haze) when running with DINP compared with DEHP (Biltrite 2005). DINP’s processability is similar to DEHP’s.

Exposure to DINP during processing or use of resilient flooring is expected to be minimal due to the lower emissions relative to DEHP. During use there is little likelihood of DINP migrating out of the polymer matrix and causing exposure. In the event that humans do become exposed to DINP from this use however, there may be associated health effects.

Workplace air exposure standards have not been established for DINP, which although considered an animal carcinogen, has not been completely classified as to human carcinogenicity (CDC 2005).

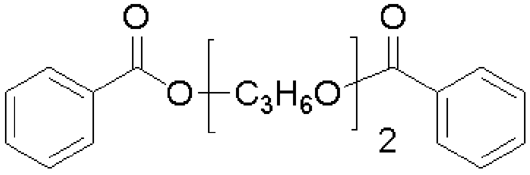
According to the Chronic Health Advisory Panel, exposure to DINP results in potential acute toxic effects (Chronic Hazard Advisory Panel (CHAP) 2001). The NOAEL for systemic toxic effects induced in laboratory animals by exposure to DINP is estimated between 15 mg /kg bw/d and 88 mg/kg bw/d. To put this into context, a study by the Consumer Council Austrian Standards Institute (Fiala n.d.) used the lowest NOAELs for DINP and DEHP to determine a total daily intake level for these plasticizers (this study focused on the use of DINP and DEHP in children’s toys that would be mouthed, using a risk factor of 100) of 150 μg/kg bodyweight /day for DINP and 37 μg/kg bodyweight /day for DEHP. Based on this study, DINP is less toxic than DEHP.

According to its review of relevant studies, the CHAP concludes that DINP is clearly carcinogenic to rodents, inducing hepatocellular carcinoma in rats and mice of both sexes, renal tubular carcinoma in male rats, and mononuclear cell leukemia in male and female rats. The studies they reviewed also suggest possible carcinogenicity in the testis, uterus, and pancreas in rodents (CHAP 2001). DINP has not been categorized by EPA or IARC as to its carcinogenicity.

Dipropylene Glycol Dibenzoate (DGD)

DGD is a benzoate plasticizer with great affinity for PVC; as a result, vinyls containing DGD show good resistance to solvent extraction and perform well in volatility tests. Figure 7.4.1 E illustrates its chemical structure. The volatility of DGD is only slightly higher than DEHP, indicating relatively similar plasticizer losses and emissions during processing. The compatibility with PVC is reported as good due to a vapor pressure that is similar to that of DEHP. Velsicol Chemical Corporation makes and markets this plasticizer under the name Benzoflex® 9-88.

Figure 7.4.1 E: Chemical Structure of DGD



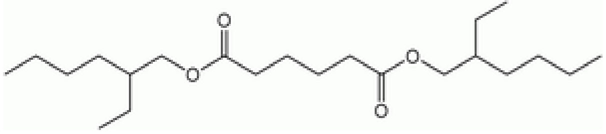
Benzoate alternative plasticizers have been known for years as effective PVC plasticizers. Although they represent effective plasticizer substitutes, benzoates, and specifically DGD, have not been widely used. Serious consideration has been revived due to the search for substitutes caused by the ongoing phthalate controversies.

DGD is estimated as persistent in sediments for 140 days, and produces a chronic aquatic toxicity at 0.55 mg/L. While neither of these levels exceed methodology thresholds, they do suggest that precaution should be used when using DGD. The primary routes of exposure potentially associated with DGD are inhalation and dermal. According to the MSDS for this product, there is virtually no human toxicity anticipated based on rodent studies (Velsicol Chemical Corporation 2002). They estimate an oral LD50 of greater than 5000 mg/kg. However, this product does have a Risk Phrase of R-51/53 associated with it, indicating that it may cause long term toxic effects in the aquatic environment[24]. The MSDS also indicates that there may be irritation associated with inhalation, ocular and dermal contact to DGD. DGD is not a listed carcinogen, nor is there a specific water quality criterion established for this chemical.

Di (2-Ethylhexyl) Adipate (DEHA)

DEHA is an adipate plasticizer whose specific chemical structure is shown in Figure 7.4.1 F. Adipates are classified as low temperature plasticizers and are all relatively sensitive to water (DEPA 2001). Its low temperature properties make DEHA a potentially favorable plasticizer for materials used to store cold solutions (*e.g.,* blood). DEHA is less compatible with PVC than DEHP, which can lead to exudation (*i.e.,* plasticizer migrating to the surface). DEHA is known to be slightly more difficult to process compared to DEHP, though it exhibits relatively lower volatility than DEHP.

Figure 7.4.1 F: Chemical Structure of DEHA



The Danish EPA determined that DEHA has the potential to migrate from the PVC matrix into fatty solutions. They conducted a review of toxicological data associated with a number of plasticizers, including DEHA. A NOAEL of 610 mg/kg bodyweight/d has been reported (DEPA 2001), which is orders of magnitude higher (*i.e.,* indicating lower toxicity) than the NOAEL for DEHP. However the Institute did not determine if any studies evaluating the impact of exposure on the male reproductive system have been conducted. The Chronic Health Advisory Panel for the US Consumer Product Safety Commission quotes a study that indicates a fetotoxicity issue associated with oral exposure to DEHA (CHAP 2001).

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[24] Note that DEHP has risk phrases of R-60 and 61, which indicate may impair fertility and may cause harm to the developing fetus, respectively

Summary of Plasticizer Alternatives Assessed for Resilient Flooring

Table 7.4.1 C summarizes the comparative assessment of plasticizer alternatives to DEHP for use in PVC resilient flooring. Refer to Table 7.3.1 B for associated data.

Table 7.4.1 C: Summary of Plasticizer Alternatives Assessment for Resilient Flooring

Assessment Criteria		**DEHP (Reference)**	**Comparison Relative to DEHP**			
			DEHT	**DINP**	**DGD**	**DEHA**
Technical/ Performance Criteria	Volatility	**1.4×10^{-6} mm Hg**	-	+	=	+
	Compounding	**Good**	?	=	=	=
	Tensile Elongation (life of product)	**MW 390**	=	=	=	=
	PVC Compatibility	**Good**	=	=	=	-
	Loss of Plasticizer (Manufacture, Use)	**Acceptable** (M, U)	=	= (M) - (U)	=	-
Cost	Cost /lb applied	**$0.70** (March 2006)	=	=	=	=
Environmental Criteria	Persistence	**Sediment** (140 days)	=	=	=	+
	Bioaccumulation	**BCF = 310**	+ (BCF = 25)	+ (BCF = 3.2)	+ (BCF = 190)	+ (BCF = 61)
	Aquatic (Fish) Toxicity	**> 0.0025 mg/l**	= (>0.015 mg/L)	= (>0.14mg/L)	= (0.55 mg/L)	+ (>100 mg/L)
Human Health Criteria	Carcinogen	EPA **B2**, IARC **3**	?	= (indicated in rodents – *CHAP 2001*)	?	?
	Reproductive Toxicity	**Yes** (Prop 65, EU; NOAEL = 3.7 - 100 mg/kg bw/d)	+	+	+	= (pot. feto toxicity)
	Occupational Exposure to Emissions (mfg)	**Yes**	=	=	?	-
	LD50	**34 g/kg**	?	+	+	-
	Irritation	**Yes** (Dermal, Ocular, Respiratory)	= (D,O) + (R)	+	=	+ (D) = (O,R)

Comparison Key + Better = Similar - Worse ? Unknown

Material Alternatives for DEHP/PVC Resilient Flooring

Flooring Material Alternative #1: Natural Linoleum

A natural product is a non-petroleum based, biodegradable product. Linoleum products are typically available in sheet and square form. While natural linoleum can be found in hundreds of colors and patterns (see Figure 7.4.1 G), there are currently fewer choices than for DEHP/PVC.

Figure 7.4.1 G: Typical Color Choices for Linoleum

Source: *Marmoleum 2006*

Construction

Natural linoleum is made from linseed oil, wood flour, resin, jute and limestone and calendared onto a natural jute backing. The table below lists materials commonly used in natural linoleum.

Table 7.4.1 D: Composition of Natural Linoleum Flooring[25]

Wt. %	Material	Origin/Precursor Materials
30	Wood powder	From wood sawdust, provides the unique characteristic of being able to bind with pigment; gives linoleum products colors and ensures long-term color-fastness.
25	Linseed oil	Obtained by pressing the seeds of the flax plant are linoleum's most important raw material (and the origin of its name).
20	Limestone	Found all over the world in large quantities; used in very finely ground form.
10	Jute	Spun from the fibers of jute plants in India and Bangladesh, it is the preferred backing of many natural linoleum products.
5	Resin	Typical resin sources include pine and spruce trees. Other resins include balsam or copal resins Balsam resin is obtained in a similar way to rubber, by tapping from plantation trees. Copal is a fossilized resin found in the ground in wooded environments in Africa, South America and Asia.
5	Cork flour	Ground bark of the cork oak. The bark is peeled every seven to ten years without damaging either the lifespan or the health of the tree.
5	Pigments	Manufacturers typically avoid the use of heavy metals pigments such as lead, hexavalent chromium and cadmium.

Installation/Cleaning/Maintenance

Professional installation is recommended since over 95% of reported complaints are due to faulty installation (Forbo Holding 2006). Most manufacturers offer a line of finishing and cleaning products. Manufacturers recommend that natural linoleum flooring be protected with a wax type finish or polish 2-3 days after installation. Everyday cleaning includes keeping floor dirt-free with a dry dust mop and/or dust cloth and spot removal with a neutral cleaner and damp cloth.

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[25] Sources: Gunther and Langowski1997; Forbo Holding 2006, Armstrong, Inc. website (www.armstrong.com/resflram/na/linoleum/en/us/)

Financial

Natural linoleum's cost depends not only on the product and design, but also on the quantity of product purchased (as volume discounts are often available). Installation costs will vary according to contractor and location. Natural Linoleum flooring is expected to last between 25 and 40 years.

Table 7.4.1 E: Typical Costs Associated with Linoleum Flooring

Total Cost ($/ft^2)	Material ($/ft^2)	Installation ($/ft^2)
~5.00	2 to 2.50	2.5

Environmental and Human Health Issues

The chief environmental impact associated with natural linoleum is eutrophication from the use of nitrogen and phosphate fertilizers used to grow linseed. However the amount of eutrophication depends upon the growing conditions. For example, flax in the US is primarily grown in North Dakota in 3 to 6 year rotations with other crops and requires no added nitrogen. VOCs, generated during the manufacturing process, are another concern with linoleum. While most VOCs are emitted during the manufacturing and drying process, residual VOCs can off gas following installation.

Other manufacturing-related pollution includes energy combustion and the associated greenhouse gases, particulate emissions and other air pollutants. Like DEHP/PVC, installation involves the use of water-based styrene butadiene floor adhesives. Linoleum is not recyclable but is compostable, however there is no infrastructure to collect and compost it at the end of life.

Table 7.4.1 F: Environment and Human Health Issues Associated with Natural Linoleum

Life Cycle Phase	Environment and Human Health Issues	Positive Aspects of Natural Linoleum
Raw Materials	• Eutrophication and global warming impacts from the use of nitrogen based fertilizers to cultivate flax • Sustainability of natural ingredients not assured • Does not contain recycled content • Manufactured in Europe • No recycled content	• Derived from natural ingredients
Manufacture	• Energy use and associated greenhouse gas, particulate and other related emissions. • VOC generation during the manufacturing process	
Installation	• Styrene butadiene floor adhesive off-gas VOCs • Surface topcoat of acrylic usually applied	
Use and Maintenance	• Cleaning, waxing VOC off gassing potential	• Can be cleaned with a mild detergent
End of Life	• Not recyclable • Compostable but no infrastructure	• Biodegradable raw materials • Compostable • No chlorine products generated if incinerated

Environment, Health, and Safety Comparison of DEHP/PVC and Linoleum

There are numerous fact sheets and studies comparing linoleum and DEHP/PVC flooring. Studies and reports that use a hazards based analysis rank linoleum as safer than both VCT and vinyl sheet, citing the hazards of PVC precursor chemistry, plasticizers, and dioxin formation in manufacture and end-of-life combustion under suboptimal conditions. Studies based on life cycle generally conclude that linoleum has comparable or slightly fewer environmental impacts when compared with PVC sheet flooring of equivalent quality in the production phase (VBD 2004). Several studies point to the importance of detergent or chemical use in cleaning and maintenance, since across the useful life of the product the use of the associated maintenance chemicals/materials can lead to significant impacts (VBD 2004). One study that focuses solely on the use phase suggests that in PVC might have advantages over linoleum in this phase. This result is dependent on the frequency of cleaning, and type of cleaning (wax or polish) process used (Paulsen 2003). However this study did not examine indoor air quality issues. Regardless of the floor type (*e.g.,* DEHP/PVC or linoleum), wax-based systems are preferable to polish systems in many applications (Paulsen 2003). Higher quality products that require less use phase maintenance can significantly lower life cycle impacts (VBD 2004). The forthcoming US Green Building Council combined life-cycle risk assessment of VCT, vinyl sheet, linoleum and cork should provide additional insight into the tradeoffs between these materials.

Table 7.4.1 G: Summary of Comparison between DEHP/PVC and Linoleum

Life Cycle Assessment	Hazards Analysis
• Linoleum has comparable or lower environmental impacts compared to DEHP/PVC flooring of equivalent quality in the production phase. • In the use phase, the differences between DEHP/PVC and linoleum will depend more on the cleaning regime used more than the flooring material.	• Strong preference for natural linoleum over DEHP/PVC tile and sheet flooring

Flooring Material Alternative #2 - Natural Cork

Cork oak trees grow in forests in Portugal, Algeria, Spain, Morocco, France, Italy and Tunisia (Jones 1999). Bark is first stripped when trees are roughly 25 years old and approximately every nine years thereafter. No more than 50% of the bark is removed, and most cork oak trees survive many generations. After being removed from the tree, workers cut large slabs into strips that are stored in the forest for seven months or more to cure (Expanko 2006).

After harvest, the best cork is punched out to make bottle stoppers. The remaining is ground into granules, combined with binders, and baked in molds. Various temperatures produce different colors of cork and dyes are never used for coloring. To produce floor tiles, the blocks of baked cork are cut into slabs, sanded and varnished. Color variations are achieved by varying baking temperature (Jones 1999). Table 7.4.1 H lists the main constituents in cork flooring and their origins or component materials.

Table 7.4.1 H: Composition of Cork Flooring

Material	Origin/Precursor Materials
Cork granules	Cork oak trees
Binders	Urea-formaldehyde, urea melamine, phenol formaldehyde, polyurethane, or natural proteins

Installation/Cleaning/Maintenance

Any experienced hardwood and /or ceramic tile flooring installer can install cork (Expanko 2006). Regular cleaning includes vacuuming and light cleaning with a damp sponge mop. Ammonia-based cleaners or chemicals must not be used to clean cork floors. For routine care, sweep or vacuum to remove lose dirt before it can scratch or be ground into the floor's surface.

Financial

Cork's cost depends not only on the product and design, but also on the quantity of product purchased (as volume discounts are often available). Installation costs will vary according to contractor and location. Current cost estimates for cork flooring are:

Cost of material (per square foot):	$4 - $6
Installation (per square foot):	$ 6
Overall cost (per square foot):	$10 - $12

Cork flooring is expected to last up to 80 years, which should factor into its overall cost when compared to other materials.

Environmental and Human Health Issues

There are relatively few environmental impacts associated with the growing and harvesting of cork. No fertilizers or pesticides are used to promote tree growth or kill pests. Cork forests are managed carefully in many countries (Jones 1999). The main issue associated with cork flooring manufacturing is the binders use to hold together the cork granules. Binder types include urea-melamine, phenol-formaldehyde (see Chapter 4 for discussion of EH&S issues associated with formaldehyde binders), or polyurethane.

During the installation phase, indoor air quality problems can exist with the adhesives, finishes, or sealers used. Both water-based and polyurethane-based adhesives are used. Cork is also finished similarly to wood, using wax or polyurethane. Off-gassing will depend on the type of finish applied. Pre-finished cork tiles are on the market, eliminating the need for on-site finishing, but this results in a lack of sealing around the individual tile joints (Jones 1999). Unlike with other floorings, cork can be installed as a floating floor, with no adhesive use required.

Table 7.4.1 I: Environment and Human Health Issues Associated with Cork

Life Cycle Phase	Environment and Human Health Issues	Positive Aspects of Cork
Raw Materials	• Binder manufacture • Cork imported from Spain, Portugal and Africa	• Very few impacts associated with cork growing and harvesting • Renewable resource
Manufacture	• Worker exposure to binders	
Installation	• Off-gassing of adhesives	
Use and Maintenance	• Off-gassing of polyurethane maintenance coatings	• Hypoallergenic
End of Life	• Not recyclable • Compostable but no infrastructure	• Compostable • No chlorine products generated if incinerated

Environment, Health, and Safety Comparison of DEHP/PVC and Cork

There are numerous fact sheets and studies comparing cork and DEHP/PVC flooring. Studies and reports that use a hazards based analysis rank cork as safer than both VCT and vinyl sheet, citing the hazards of PVC precursor chemistry, plasticizers, and dioxin formation in manufacture and end-of-life combustion under sub-optimal conditions.

A combined life-cycle risk assessment of VCT, vinyl sheet, linoleum and cork has been conducted by Georgia Technical Research Insitute (Jones 1999) using the EPA BEES (Building for

Environmental and Economic Sustainability) software. It is an extensive assessment that can be viewed at the Georgia Tech website[26]. In general, it indicates that cork has a better life cycle profile than the vinyl flooring alternatives. Another study compared cork flooring to cork finished with a PVC top laminate to protect the cork surface. This study found that cork flooring with a PVC top laminate had significantly higher ecological impacts than cork without the laminate, even if cork polyurethane refurbishing interval was assumed to be every 2 years (Althaus and Richter 2001).

Table 7.4.1 J: Summary of Comparison between DEHP/PVC and Cork

Life Cycle Assessment	Hazards Analysis
Cork exhibits better life cycle impact profile than VCT	Strong preference for cork over DEHP-PVC tile and sheet flooring.

Flooring Alternative #3 – Polyolefin Flooring

A combination of synthetic copolymer resins and limestone, this material is manufactured by Amtico Company, based in Coventry, United Kingdom, under the name Stratica. This flooring material was specifically designed for large, high-traffic commercial areas and is used in health care facilities, ships, shopping centers, and airports. According to the Stratica website[27], the product offers the convenience and durability of DEHP/PVC flooring and is easy to install.

Construction

Polyolefin flooring consists of two layers of polymers. The bottom layer is made from ethylene copolymers and includes chalk and clay as filler materials. The top layer consists of an ionomer coating called Surlyn™, created from ethylene/methacrylic acid copolymers.

Table 7.4.1 K: Composition of Polyolefin Flooring

Material	Origin/Precursor Materials
Polyethylene	Ethylene from natural gas or oil
Chalk	Abundant naturally occurring mineral
Clay	Abundant naturally occurring mineral
Suryln	Ethylene/methacrylic acid

Source: *Fisher 1999*

Installation/Cleaning/Maintenance

Polyolefin flooring is installed using VOC-free adhesives. Cleaning and maintenance are simple. Flooring can be swept or vacuumed and mopped with water when necessary. Amtico says the flooring is scuff-resistant and that in abrasion tests, it performed 10 times better than linoleum, and twice as well as quality vinyl tiles and laminates (Fisher 1999).

Financial

Polyolefin flooring comes in a variety of patterns that mimic natural flooring, including solids, marbles, granites, stones, terrazzos, and woods. Polyolefin flooring is priced slightly higher than high-end vinyl flooring. The manufacturer claims that the cost savings in installation and maintenance over the long term result in significant overall cost saving. Purchase and installation

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[26] http://maven.gtri.gatech.edu/sfi/resources/pdf/TR/Resilient_flooring.pdf

[27] www.stratica.com

costs are estimated to be $5 to $6 per square foot. The lifespan of polyolefin flooring is anticipated to be higher than DEHP/PVC flooring, though less than that of cork (Lent 2006).

Environmental and Human Health Issues

The chief environment and human health issues associated with polyolefin center around the extraction and processing steps. Impacts include extraction and refining of ethylene and mineral feedstocks and the greenhouse gas and other air pollutants associated with these activities. One of the chief benefits of polyolefin flooring is during the use phase due to its durability and ease of maintenance. Polyolefin flooring can be cleaned with a mild detergent. No polishing or waxing or other finishing (unlike DEHP/PVC tile and sheet, linoleum or cork) is required. In addition, unlike DEHP/PVC tile and sheet and linoleum, polyolefin flooring has very low VOC emissions associated with it once installed.

Table 7.4.1 L: Environment and Human Health Issues Associated with Polyolefin Flooring

Life Cycle Phase	Environment and Human Health Issues	Positive Aspects of Polyolefin
Raw Materials	• Extraction and refining of petroleum based feedstocks • Ethylene feedstock is non-renewable • No recycled content	
Manufacture	• Energy use • Associated greenhouse gas, particulate and other related emissions	
Installation	• Styrene butadiene floor adhesive off gas VOCs	
Use and Maintenance		• Can be cleaned with a mild detergent • No polishing or waxing required • Very low VOC emissions
End of Life	• No recycling infrastructure in place	• Recyclable • No chlorine products generated if incinerated

Environment, Health, and Safety Comparison of DEHP/PVC and Polyolefin Flooring

There are several green building websites and fact sheets comparing polyolefin and DEHP/PVC flooring. Studies and reports that use a hazards-based analysis rank polyolefin preferably to VCT and vinyl sheet, citing the hazards of PVC precursor chemistry, plasticizers, and dioxin formation in manufacture and end-of-life combustion under sub-optimal conditions. According to Environmental Building News, the German Frauenhoffer Institute prepared a LCA comparing polyolefin and vinyl flooring. It appears that this is the only LCA study on polyolefin flooring that has been conducted to date. The study found that the production of polyolefin flooring requires 30% less energy and 29% less water than the production of vinyl, resulting in 33% less contribution to global warming and 54% less acidification (Healthy Building Network (HBN) 2005). The Institute was unable to independently review the Frauenhoffer study to examine boundary conditions and other important study assumptions.

Summary of Material Alternatives Assess for Resilient Flooring

Table 7.4.1 M summarizes the Institute's assessment of material alternatives to DEHP/PVC resilient flooring.

Table 7.4.1 M: Materials Alternatives Assessment Summary for Resilient Flooring

Assessment Criteria		DEHP/PVC Reference	Comparison of Materials to DEHP/PVC		
			Linoleum	Cork	Polyolefin
Performance Criteria	Color/Pattern Choices	**Large**	=	-	=
	Ease of Maintenance	**Easy**	=	=	=
	Recyclable	**Yes**	-	-	=
Cost	Purchase and Installation Cost	**$2 - $10/ft^2**	=	=	=
	Expected Lifespan of Material	**25+ years**	+	+	+
Environmental Criteria	Derived from Sustainable Material	**No**	+	+	=
	Use Environmentally Preferred Materials for Installation	**Possible**	=	+	=
	Energy Use/ GHG emissions (mfg)	**Ref .**	+	?	=
	Biodegradable/ Compostable	**No**	+	+	=
Human Health Criteria	Emissions of VOCs • Manufacture • Installation • Use	**Yes (M, I, U)**	=	=	= (M, I) + (U)

Comparison Key + Better = Similar - Worse ? Unknown

7.4.2 Alternatives Assessment for Medical Devices for Neonatal Care: Sheet and Tubing Applications

PVC is widely used as a plastic in medical sheet and tubing type devices. Studies suggest that as much as 25% of all plastics used in hospital environments are PVC. Regardless of the material or plasticizer used in a medical device, however, there are certain characteristics that are desirable for these applications.

Figure 7.4.2 A, created by BASF[28] illustrates a common use of both sheet and tubing in medical applications, in this case enteral feeding.

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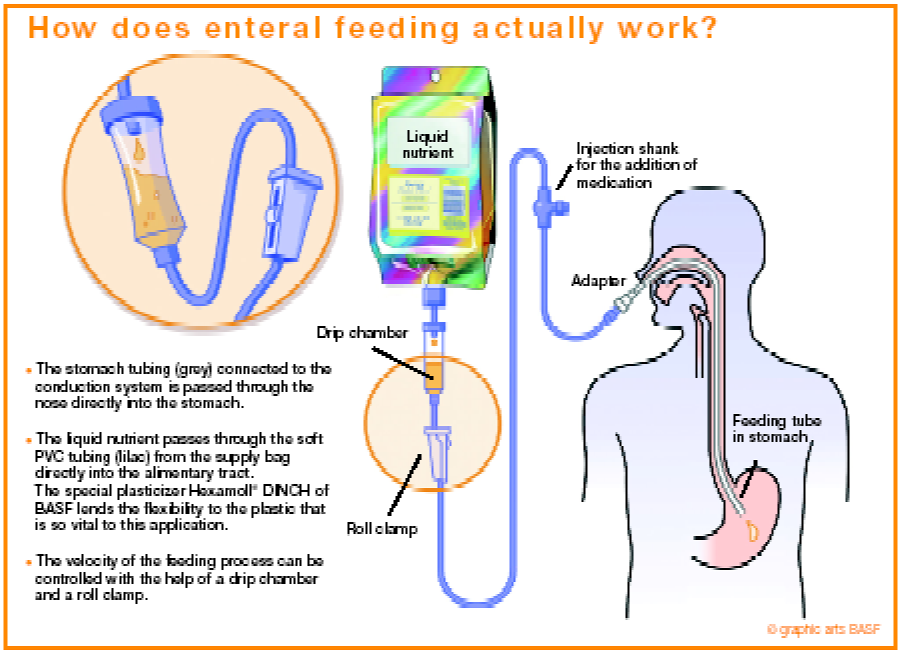
[28] Go to www.corporate.basf.com and click on "Science Around Us"

Figure 7.4.2 A: Example of medical sheet and tubing application



How does enteral feeding actually work?

- The stomach tubing (grey) connected to the conduction system is passed through the nose directly into the stomach.
- The liquid nutrient passes through the soft PVC tubing (lilac) from the supply bag directly into the alimentary tract. The special plasticizer Hexamoll® DINCH of BASF lends the flexibility to the plastic that is so vital to this application.
- The velocity of the feeding process can be controlled with the help of a drip chamber and a roll clamp.

© graphic arts BASF

Technical Considerations for Medical Devices in General

Medical devices used in neonatal procedures include bags used to store a variety of medical solutions, and tubing used to transfer those solutions to the neonate.

An interesting issue associated with DEHP as the plasticizer is that it apparently functions as an inadvertent preservative for blood platelet storage. It is now well established that red blood cells can be stored for up to 72 hours in DEHP plasticized blood bags. The required shelf life of red blood cells in storage is a 75% survival for 24 hours after infusion on the last day of storage. DEHP improves red blood cell storage by reducing haemolysis and membrane loss (Hill et al. 2001). The result is that red blood cells stored in PVC bags plasticized with DEHP have a shelf-life of up to 42 days (American Association of Blood Banks (AABB) 2006). Baxter, the leading manufacturer of blood bags in the United States, introduced a non-DEHP PVC red blood cell bag in 1991 (Plastics Week 1992). That bag, plasticized with butyryl-trihexyl citrate (BTHC) performs as well the DEHP bag, with the same shelf life as the DEHP bags (Food and Drug Administration (FDA) 1999).

One study looked at the effect of DEHP plasticizer on stored platelets (Racz and Baroti1995). They found that platelet aggregation was the only parameter that was slightly inhibited in DEHP-plasticized bags indicating that the presence of DEHP had no harmful effect during storage especially if bags are manufactured to assure higher gas permeabilities. However, the majority of platelets used in the US today are stored in non-DEHP bags. For platelets, a 40% recovery after 72 hours of storage is generally considered acceptable (FDA 1999).

In vitro studies showed that DEHP reduced platelet functions such as aggregation responses and the percentage of hypotonic shock responses. It also prevented morphological changes in platelets which are frequently seen in TOTM and BTHC plasticized PVC bags (Racz and Baroti 1995). These changes have been explained on the basis of the migration of DEHP into the plasma stabilizing platelet membrane and thereby preventing changes. This apparent preservative function seems to only be a factor in the storage of blood platelets, and therefore will not be described in more detail here.

Characteristics that are important to consider for medical device applications include aesthetic properties and physical properties. Desirable aesthetic properties of materials used in medical devices include color, clarity and odor. When choosing a material for medical devices it is important to also consider tensile strength, cold flexibility and elastic recovery. In addition, the choice of material or plasticizer must consider post manufacture technical issues, primarily its ability to withstand harsh sterilization procedures.

Aesthetic Properties of Medical Devices

Color is considered important in that it conveys "purity of product" to the user. Plasticizers are therefore more desirable if they result in colorless compounds and articles. PVC additives that produce materials that are semi-opaque or yellow in appearance may be perceived by medical staff and hospitals to be imperfect or contaminated.

In general, medical device manufacturers and users prefer that the devices be colorless and clear or transparent. Transparency allows for the end user to see the contents of any article or device made from the material, which is not only important from a perception standpoint, but also from a safety standpoint, so that medical staff can visually confirm that they have the solution they intend to be using, that the amount they need is present, and that there are no obstructions or contaminants present.

For the purposes of this assessment the Institute focused its assessment of aesthetic properties purely on color and clarity.

Physical Properties of Medical Devices

For medical device manufacturing, the design of the device must consider physical properties that influence processing and use.

Medical device materials need to have sufficient tensile strength to ensure that the article remains durable and intact throughout its intended service life. Issues can arise around potential mishandling or inappropriate storage of the device. Therefore the tensile strength of the material used should be sufficient to allow the medical device to be maintained throughout the intended service life of the product.

The material needs to retain its flexibility at low temperatures, as products are likely to be used or stored in low temperature environments. In particular, blood storage must be maintained at temperatures ranging from 2°C (for whole blood and red blood cells) to 20°C (for platelets) when not in use. The cold flexibility of the material needs to be maintained throughout the service life of the product to avoid breakage due to embrittled materials.

The rate or degree at which a material returns to its original shape after being deflected – its elastic recovery – is another important physical property of a medical device for many applications, though especially in flexible PVC tubing (*e.g.,* for use in peristaltic pumping applications). The possibility of a kink developing in a tubing device could result in inefficient delivery of the intended medical solution thereby potentially endangering the health of the patient.

One of the primary considerations of choice of plasticizer or material for medical devices relates to its ability to be sterilized as a whole unit. Sterilization of medical devices must reach 121°C to meet FDA criteria (for IV solutions), and is done through three basic mechanisms: gamma radiation, ethylene oxide and steam (autoclaving). Another sterilization process used by some healthcare facilities is electron beam sterilization, however this is much less widely practiced. Specific considerations associated with sterilization using the three primary mechanisms are summarized in Table 7.4.2 A.

Table 7.4.2 A: Medical Device Sterilization Requirements

Sterilization Mechanism	Functional Requirements
Gamma Radiation (R)	• The plasticizer should be sufficiently stable towards the energy disposition associated with the radiation sterilization process. • No sweating should occur
Ethylene Oxide (EO)	• The plasticizer should be sufficiently stable towards the heat, humidity and chemicals associated with the ethylene oxide sterilization process. • No sweating should occur
Steam (S)	• The plasticizer should be sufficiently stable towards the heat and humidity associated with the steam sterilization process. • No sweating should occur. • A low vapor pressure is desirable so the plasticizer does not distil away.

Designing a medical device to withstand the sterilizing conditions it will likely be subjected to is essential.

When evaluating plasticizers for PVC, it is also important to consider the potential of the plasticizer to migrate out of the PVC matrix and interact with the substance (*e.g.,* drug, blood, solution) that it will come into contact with. As mentioned previously, DEHP does interact with blood platelets, resulting in a preservative effect. The United States Pharmacopoeia (USP) has created standards that devices must adhere to in order to minimize the potential for undesirable migration into the medical solution. Plasticized materials must meet USP[29] Class VI standards[30]. The goal is to avoid any adverse impact on drug efficiency, and to minimize the potential for the plasticizer to migrate into the substance, thereby entering the body during use. Because of this issue, DEHP/PVC is generally not recommended for packaging certain medications with high lipid content (*e.g.,* Taxol).

Financial Considerations for Medical Devices in General

Several companies market DEHP-free products in the US. In general, the cost of the non-DEHP devices is greater than that of DEHP-containing devices. The status of relative costs may change as the demand for DEHP-free products increases. In addition, some of the alternative materials to DEHP/PVC may have longer shelf lives or allow for multiple usage that would result in an overall cost savings over time. When evaluating alternative plasticizers or materials it is valuable to consider both the raw material costs, the cost savings from increased shelf life and multiple usage, as well as the impact on usage costs such as modified sterilization requirements. Because most of this

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[29] United States Pharmacopoeia is a private (non-governmental) organization that "promotes the public health by establishing state-of-the-art standards to ensure the quality of medicines and other health care technologies." Those standards include in vivo animal biological reactivity tests for "elastomerics, plastics and other polymeric material with direct or indirect patient contact."

[30] USP Monograph 88 describes the classification of plastics into six classes based on responses to a series of *in vivo* tests for which extracts, materials and routes of administration are specified. Class VI requires the most stringent testing of the six classes. Although USP Class VI testing is widely used and accepted in the medical products industry, some view it as the minimum requirement a raw material must meet to be considered for use in health care applications. USP Class VI testing does not fully meet any category of ISO 10993-1 testing guidelines currently used by the US FDA (General Program/Bluebook Memorandum G95-1) for medical device approval.

information is proprietary, anecdotal or situation-specific, this assessment does not address economic considerations in detail.

Environmental and Human Health Considerations for Medical Devices in General

The primary concerns associated with the use of DEHP in medical devices for neonatal care is its ability to migrate out of the polymer matrix resulting in a direct exposure to a very vulnerable population. Once exposed to DEHP, the human body metabolizes it into chemicals that, along with DEHP, exhibit potential reproductive toxicity, particularly in males. In fact, in its 2002 Public Health Notification the Food and Drug Administration recommended that health providers consider using alternatives to DEHP-containing medical devices when high-risk procedures are to be performed on male neonates, pregnant women who are carrying male fetuses, and peripubertal males (FDA 2002). When assessing alternative plasticizers, the ability of the plasticizer to migrate, or exude, out of the polymer matrix is particularly pertinent, as is assessing the potential additional effect of metabolites on the neonate.

Specific Plasticizer Alternatives Assessed for Medical Devices

Plasticizer alternatives that were prioritized for medical devices include TOTM, DEHA, BTHC, and DINCH. These plasticizers represent a trimellitate, an adipate a citrate and a carboxylate, which are discussed in more detail below. A short discussion of the technical, economic and environmental, health and safety attributes will be presented for each alternative, then the information for all alternatives will summarized and compared.

Sheet Devices

In its 2000 report entitled “Use of DEHP in PVC Medical Devices: Exposure, Toxicity and Alternatives”, the Lowell Center for Sustainable Production reports that the medical sheet or bag market can broadly be divided it into three use categories: 1) IV solution, 2) blood, and 3) other bags, such as collection and specimen bags. IV bags represent the largest end-use, with 55% of the U.S. PVC medical bag market, followed by blood bags (25%) and other bags (20%) (Tickner 2000).

Based on our alternatives prioritization process, the following plasticizers were assessed for medical sheet device applications: TOTM, DEHA, BTHC and DINCH. The following is a summary of these plasticizer alternatives, focusing on the associated technical, cost (when available and not addressed previously) and EHS considerations.

TOTM

TOTM (trioctyl trimellitate, or tri (2-ethylhexyl) trimellitate) is a clear oily liquid that is a high production volume[31] plasticizer in the US. Its specific chemical structure is shown in Figure 7.4.2 B.

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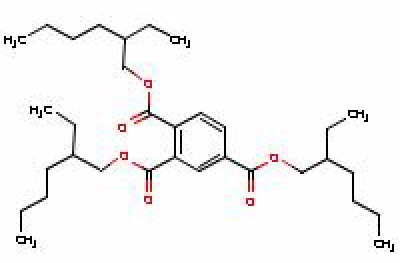
[31] Production exceeds 1 million pounds per year.

Figure 7.4.2 B: Chemical Structure of TOTM



TOTM is manufactured in the US by BASF under the brand name Palatinol®. According to the manufacturer, the performance of TOTM as a PVC plasticizer is similar to DEHP. TOTM is significantly less volatile than DEHP, which potentially results in less occupational exposure to fugitive emissions during manufacture. TOTM is therefore used in applications where low volatility is desirable.

TOTM has good PVC compatibility and is resistant to extraction by soapy water (an indication of its lipid solubility). In addition, TOTM plasticized bags possess sufficient gas permeability to be suitable for storage of platelets for over 72 hours (Nair 2002). In the medical device industry, TOTM is currently used primarily in blood and bag infusion sets. While one study reported that trimellitates migrate to the blood faster than DEHP (Yin et al. 1999), the majority of other studies reviewed found that it was more difficult to exude TOTM into lipid-soluble solutions than DEHP.

The manufacturer's literature refers to the cost of TOTM as "relatively low" and March 2006 data obtained from an industry source indicates that the cost is approximately 1.5 times that of DEHP (Teknor Apex 2005). According to the Danish Study, the price of TOTM was significantly lower than they expected. It is not expected that the cost of TOTM will be an insurmountable issue in the use of medical devices.

An industry consortium in Japan conducted a review of data available on the environmental and human health impacts of TOTM in 2002 (*Organization for Ecocnomic Cooperation and Development (OECD) 2002*)[32]. This evaluation indicated that TOTM exhibits weak toxicity in aquatic environments, and may pose a reproductive toxicity concern as evidenced by exposure to male rats. The primary routes of human exposure to TOTM during manufacture are anticipated to be via dermal contact or inhalation of mist. However studies have shown that TOTM is difficult to extract from its polymer matrix (OECD 2002) and is therefore not expected to present a significant exposure concern for patients for whom medical devices containing TOTM are used.

DEHA

DEHA is an adipate plasticizer whose specific chemical structure is shown in Figure 7.4.1F. Adipates are diesters of aliphatic dicarboxylic acids and are produced with varying alcohol groups. The low-temperature properties of DEHA potentially make it a favorable plasticizer for materials used to store cold solutions (*e.g.,* blood). DEHA is known to be slightly more difficult to process compared with DEHP.

DEHA is less compatible with PVC than DEHP, which can lead to exudation (*i.e.,* plasticizer migrating to the surface), increasing the potential for DEHA to enter the medical solution and, through use, the patient's body. The Danish EPA determined that DEHA has the potential to

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[32] The "Screening Information Data Set" (SIDS) program operated under the auspices of the Organization for Economic Cooperation and Development (OECD) is a voluntary cooperative international testing program that began in 1989

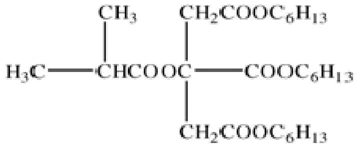
migrate from the PVC matrix into fatty solutions. They conducted a review of toxicological data associated with a number of plasticizers, including DEHA. The most sensitive population potentially exposed to DEHA as a plasticizer in medical devices is neonatal patients (as it is with DEHP). A NOAEL of 610 mg/kg bw/day has been reported (DEPA 2001), which is less toxic than the NOAEL for DEHP. However the Institute did not identify any studies evaluating the impact of exposure on male reproductive system. The Chronic Health Advisory Panel for the US Consumer Product Safety Commission quotes a study that indicates a fetotoxicity issue associated with oral exposure to DEHA (CHAP 2001).

The primary metabolite associated with human exposure to DEHA is 2-ethylhexanoic acid (EHA). The Institute did not identify any specific health hazards associated with exposure to EHA.

BTHC

Butyryl trihexyl citrate (BTHC) is a higher molecular weight plasticizer specifically designed for use in medical articles especially blood storage bags. The chemical structure of BTHC is shown on Figure 7.4.2 C.

Figure 7.4.2 C: Chemical Structure of BTHC



$$\begin{array}{lll} & \mathrm{CH_3} & \mathrm{CH_2COOC_6H_{13}} \\ & | & | \\ \mathrm{H_3C}— & \mathrm{CHCOOC} & —\mathrm{COOC_6H_{13}} \\ & & | \\ & & \mathrm{CH_2COOC_6H_{13}} \end{array}$$

According to the manufacture (Morflex, Inc.), its BTHC plasticizer (Citroflex® B-6) is a component of several FDA approved blood bag systems and provides improved low temperature properties relative to the phthalate plasticizers and superior long-term stability for red blood cells. Citroflex® B-6 has low extractability into lipid media, making it particularly useful for blood products. According to Morflex, Citroflex® B-6 is a specially formulated citric acid ester for use in PVC medical articles such as tubing and IV bags where the content medium is aqueous-based. The manufacturer therefore claims that BTHC nearly duplicates the properties of DEHP for these applications[33].

According to industry experts, the cost of BTHC is significantly higher than DEHP, with raw material costs estimated at $1.15/lb (compared to DEHP's cost of $0.70/lb).

Very little information is available on this plasticizer's migration potential from the PVC matrix or on its potential health effects if patients are exposed to it. BTHC is metabolized to butyric acid, hexanol, and citrate. When exposed to butyric acid humans may experience gastrointestinal, liver and/or skin effects.

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[33] http://www.morflex.com/pdf/bul101.pdf

DINCH

Di (isononyl) cyclohexane-1,2-dicarboxylate (DINCH) is manufactured exclusively by BASF under the brand name Hexamoll®. DINCH is the hydrogenated product of the corresponding di C9 phthalate ester (DINP). Its performance characteristics in PVC are expected to be similar to the phthalate counterpart, except for having less solvency for PVC. The manufacturer of DINCH reports that it does not appreciably migrate out of the PVC matrix when used in medical devices.

Manufacturer experience indicates that the plasticizer does not alter the properties of PVC nor change its final characteristics, so that it can be processed on existing processing equipment (Sparrow 2002). Many PVC alternative materials require new production lines or extensive retrofitting, thus increasing overall costs beyond what the marketplace will bear. Processing of PVC plasticized with DINCH only requires fine-tuning the formulation and the processing temperature to achieve the same results.

In a fact sheet prepared by Eastman Chemical (Eastman Chemical Company 2004) a comparison of certain performance characteristics for various plasticizers is presented. In this technical fact sheet, Eastman shows that DINCH is comparable to DEHP and DINP in tensile strength, elongation and modulus, but that it requires more time and energy to fuse with PVC. This may be an issue for certain medical devices, however no other indication of this drawback could be found during our research.

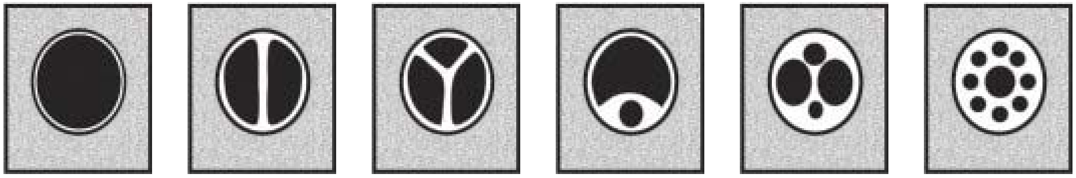
Very little information is available from the manufacturer on the cost, performance or EH&S considerations associated with DINCH, other than what has been discussed above. Other industry sources have provided a cost estimate of $0.21 more per pound than DEHP for 70 Shore A compounds. Bayreuth, a German medical device manufacturer, has switched to manufacturing its medical devices using DINCH. "If you consider the current status of the toxicological tests, then the market will likely be prepared to accept the slightly higher price. Hexamoll® DINCH offers good value for money overall," states Bayreuth's managing director Jürgen Rotter (Sparrow 2002).

In addition, by removing the aromatic ring associated with DINP, the overall toxicity associated with DINCH is expected to be reduced. BASF indicates that it has much lower potential for negative impacts on human or environmental health; consequently, BASF has introduced DINCH as a candidate for medical device applications such as for use with neonates. BASF is currently in discussions with FDA concerning submission of DINCH for approval for use in medical devices (Schaefer 2006).

Tubing Devices

Medical tubing is made from a variety of materials including metal, plastic, and synthetic rubber. Some medical tubing features diameters that measure in the thousandths of an inch, with walls thinner than a human hair. These small, specialty tubes can cost many times more than conventional high-volume tubes, but are well-suited for catheters and other medical devices that are inserted into a patient's cardiovascular system. In general, medical tubing manufacturers seek to reduce the outside diameter (OD) of their products while maintaining as large an inside diameter (ID) as possible. Figure 7.4.2 D illustrates cross-sections of some common tubing configurations.

Figure 7.4.2 D: Common configuration cross-sections of medical tubing devices



The plasticizer alternatives being assessed for tubing uses are limited to DINP and DEHA. Discussions of each chemical are found previously in this section of the report. The primary factor that delineates tubing uses from sheet uses in medical device applications is the requirement for elastic recovery.

DINP

DINP is a mixture of phthalates with branched alkyl chains of varying length (C8, C9 and C10). The chemical structure of DINP is depicted in Figure 7.4.1B.

DINP has been used as a plasticizer in medical tubing devices because it exhibits similar clarity and elastic recovery properties to DEHP.

Workplace air standards for external exposure have not been established for DINP, which although considered an animal carcinogen, has not been classified as to human carcinogenicity (CDC 2005).

When introduced into the human body, DINP is metabolized through similar mechanisms as described for DEHP metabolism. The primary metabolite for DINP is MINP (mono-isononyl phthalate). People exposed to DINP will excrete small amounts of MINP in their urine (CDC 2005). Studies of oral exposures of DINP to rats indicate that it is primarily metabolized in the body, with the majority of the un-metabolized DINP and its metabolites being excreted within days of exposure. The major routes of excretion for orally administered DINP in rats were urine and feces, with about equal amounts excreted by either route at low doses, but more excreted in feces at high doses (Midwest Research Institute (MRI) 1983). Repeated dosing caused no accumulation of DINP or its metabolites in blood or tissue, but resulted in increased formation and elimination of the monoester side-chain oxidation products (MRI, 1983).

According to the Chronic Health Advisory, exposure to DINP results in potential acute toxic effects (CHAP 2001). The NOAEL for systemic toxic effects induced in laboratory animals by exposure to DINP is estimated between 15 mg/kg bw/d and 88 mg/kg bw/d. To put this into context, a study by the Consumer Council Austrian Standards Institute (Fiala) used the lowest NOAELs for DINP and DEHP to determine a total daily intake level for these plasticizers (this study focused on the use of DINP and DEHP in children's toys that would be mouthed and used a safety factor of 100) of 150 μg/kg bw/d for DINP and 37 μg/kg bw/d for DEHP.

According to its review of relevant studies, the CHAP concludes that DINP is clearly carcinogenic to rodents. The studies they reviewed also suggest possible carcinogenicity in the testis, uterus, and pancreas (CHAP 2001). DINP has not been tested for carcinogenicity in young rodents, an important limitation with respect to this assessment, as it is exposure to the very youngest population that the Institute is focusing on for medical device applications. However, DINP has not been listed as an EPA or IARC possible human carcinogen.

DEHA

In addition to the discussion of DEHA for medical sheet uses, it is important to also consider a key performance parameter for DEHA use in tubing – elastic recovery. DEHA is reported to exhibit similar elastic recovery properties to DEHP (DEPA 2003). When exposed to the human body, DEHA can be metabolized into EHA, which does not have clearly identified human health concerns associated with it.

Table 7.4.2 B summarizes the assessment criteria associated with plasticizer alternatives to DEHP in medical devices[34].

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[34] Refer to Appendix C for the complete summation of EH&S factors associated with the various plasticizers evaluated for each use of DEHP.

Table 7.4.2 B: Medical Device Plasticizer Alternative Assessment Criteria

Plasticizer Acronym	**Performance and Cost Primary Criteria**								**Environmental Health and Safety Criteria**								
	Physical and Aesthetic Properties				Processability			**Cost** per pound (Normalized using SF)	Carcinogen	Reproductive/ Developmental Toxin	Sediment Persistence	Bioaccumulation (BCF)	Other Health Effects		Fish Toxicity (mg/L)	Migration	Metabolite of Concern
	Clarity	Tensile Elongation	Cold Flexibility	Elastic Recovery	Sterilizability	PVC Compatibility	Emission During Mfg/ Use						LD50 (oral -g/kg)	Irritation (D,O,R)			
DEHP	Exc. (Ref)	Ref (MW 390)	Good (Ref)	Slow but acceptable (Ref)	Ref	Ref	Ref	$0.70	EPA Class B2, IARC Class 3	Listed in Cal Prop 65, EU R43	140	310	34	D, O, R	No effect at 0.0025	Possible migration in lipid soluble drugs	MEHP (repro toxin)
DEHA	Exc.	Similar to DEHP MW 370-390	Good	Slow but acceptable	Similar to DEHP	Fair	Lower volatility than DEHP	$0.70	Not listed	Potential fetotoxicity *(CHAP 2001)*	78	61	5.6	O, R	>100 at 96 h	Migration probable	EHA (not known to be toxic)
DINP	Exc.	Higher than DEHP MW 418	~ better than DEHP	Slow but acceptable	Similar to DEHP; slightly more tolerant of steam than DEHP	good	M: Expected to be similar to DEHP U: Slightly less than DEHP	$0.77	Indicated in rodents *(CHAP 2001)*	Not listed	140	3.2	Unknown	No	>0.14 at 96 h	Expected to be similar to DEHP	MINP (possible repro. toxin)
DINCH	Good	Higher than DEHP MW 514	Better than DEHP	Comparable to DEHP	Unk.	good (per mfgr)	Unknown	$0.91	Not listed	Not listed	Unk.	189	>5000	No	>100 (LC50)	Manufacturer claims low	Unk.

Table 7.4.2 B: Medical Device Plasticizer Alternative Assessment Criteria

Plasticizer Acronym	Performance and Cost Primary Criteria								Environmental Health and Safety Criteria								
	Physical and Aesthetic Properties				Processability			**Cost** per pound (Normalized using SF)	Carcinogen	Reproductive/ Developmental Toxin	Sediment Persistence	Bioaccumulation (BCF)	Other Health Effects		Fish Toxicity (mg/L)	Migration	Metabolite of Concern
	Clarity	Tensile Elongation	Cold Flexibility	Elastic Recovery	Sterilizability	PVC Compatibility	Emission During Mfg/ Use						LD50 (oral -g/kg)	Irritation (D,O,R)			
DEHP	Exc. (Ref)	Ref (MW 390)	Good (Ref)	Slow but acceptable (Ref)	Ref	Ref	Ref	$0.70	EPA Class B2, IARC Class 3	Listed in Cal Prop 65, EU R43	140	310	34	D, O, R	No effect at 0.0025	Possible migration in lipid soluble drugs	MEHP (repro toxin)
TOTM	Exc.	Higher than DEHP MW 546	~ worse than DEHP	Slow	Similar to DEHP	good	Significantly lower than DEHP (M & U), by 1:5 ratio	$1.11	Not listed	Potential toxicity in male rats (*SIDS 2002*)	78	3.2	Unknown	D, O	>100 @ 96 h	Difficult to extract from polymer matrix	Unk.
BTHC	Good	Higher than DEHP MW 514	Better than DEHP	Unknown	Similar to DEHP; hydrolysis expected for steam	Probably satisfactory	Good ventilation required (M&U)	$1.12	Not listed	Mfgr literature indicates no toxic effects	78	44	Unknown	No (according to mfgr)	Not Est.	Low extractability into lipid-soluble media	Butyric acid (irritant)

Notes: D = dermal, O = ocular, R = respiratory
Refer to Table 7.4B for cost references
Environmental and human health references from Table C5 in Appendix C
Processing values primarily from Danish EPA study (DEPA 2001), as well as other industry sources

Summary of Plasticizer Alternatives Assessed for Medical Devices

Table 7.4.2 C summarizes the plasticizer alternatives assessment in comparison to DEHP for use in medical devices for both sheet and tubing applications. Recall that only DINP and DEHA were evaluated for tubing applications. Refer to Table 7.4 A for specific information associated with determining the comparative assessment of plasticizer alternatives for this application. Refer to Table 7.4.2B for other data.

Table 7.4.2 C: Summary of Plasticizer Alternatives Assessment for Medical Devices

Key Assessment Criteria		**DEHP (Reference)**	**Comparison Relative to DEHP**				
			TOTM	**DEHA**	**BTHC**	**DINCH**	**DINP**
Technical/Performance Criteria	Clarity	**Excellent**	=	=	=	=	=
	Cold Flexibility	**Good**	-	=	+	+	+
	Elastic Recovery	**Slow** but acceptable	=	=	?	=	=
	Sterilizability • Radiation • EO • Steam	**Good** (R, EO, S)	=	=	= (R,EO) - (S)	?	= (R,EO) + (S)
	PVC Compatibility	**Good**	=	-	=	=	=
	Plasticizer Loss • Manufacture • Use	**Acceptable** (M, U)	+ (M, U)	- (M, U)	- (M + (U)	? (M) + (U)	= (M, U)
Cost	Cost /lb applied (70 Shore A)	**$0.70** (March 2006)	-	=	-	-	=
Environmental Criteria	Persistence	**Sediment** (140 days)	+	+	=	?	=
	Bioaccumulation	**BCF = 310**	+ (BCF = 3.2)	+ (BCF = 61)	+ (BCF = 44)	+ (BCF = 189)	+ (BCF = 3.2)
	Aquatic (Fish) Toxicity	**> 0.0025 mg/L**	+ (>100 mg/L)	+ (>100 mg/L)	?	+ (>100 mg/L)	= (>0.14 mg/L)
Human Health Criteria	Migration (lipid-soluble)	**Yes**	+	=	+	+	=
	Occupational Exposure to Emissions (mfg)	Yes	+	-	-	?	= (M)
	Carcinogen	EPA **B2**, IARC **3**	?	?	?	?	= (indicated in rodents – *CHAP 2001*)

Table 7.4.2 C: Summary of Plasticizer Alternatives Assessment for Medical Devices

Key Assessment Criteria	DEHP (Reference)	Comparison Relative to DEHP				
		TOTM	**DEHA**	**BTHC**	**DINCH**	**DINP**
Reproductive Toxicity	**Yes** (Listed on CA Prop 65, EU R60 and R61)	= (pot. toxicity in male rats)	= (pot. feto toxicity)	+	+	+
LD50	**34 g/kg**	+	-	?	+	+
Irritation	**Yes** (Dermal, Ocular, Respiratory)	= (D,O) + (R)	+ (D) = (O,R)	+	+	+
Metabolite of Concern	**Yes** (MEHP, a reproductive toxin)	?	? (no effects identified for EHA)	= (GI, liver and skin effects associated w/ butyric acid)	?	? (no effects identified w/MINP)

Comparison Key + Better = Similar - Worse ? Unknown

Medical Device Material Alternatives

In addition to considering alternative plasticizers for PVC, there are alternative materials that would not require a plasticizer, either because they are inherently flexible, or because they fulfill the function without being plasticized. For materials that are inherently flexible, the potential for the material to become brittle due to loss of plasticizer is eliminated, therefore these materials may have longer shelf lives than their PVC-based counterparts and the possibility of leached plasticizer entering the body is eliminated (important considerations in the medical device industry). Types of alternative materials that are appropriate for medical devices and will be further evaluated include an inorganic substance (glass, which is not a flexible polymer, but the material has been used historically for many medical applications), an elastomer (silicone), a copolymer (ethylene vinyl acetate, EVA), thermoplastic olefins (polyethylene, PE, and polypropylene, PP) and a thermoplastic resins (thermoplastic polyurethane, TPU).

Manufacturers of medical devices such as Hospira and Baxter, who together command approximately 90% of the market, have been in the news lately, touting their new lines of sheet devices (*i.e.,* IV bags) that are 'PVC-free' and therefore, DEHP-free (Waldman 2006). In addition, many large hospital chains have increasingly been making purchasing decisions that include DEHP and/or PVC-free materials[35]. Therefore the availability of feasible alternatives to DEHP in PVC sheet and tubing materials for the medical device industry can be expected to continue to increase in the near future.

The performance criteria discussed for medical devices in the beginning of Section 7.4.2 also apply for material alternatives for medical devices. The following sections summarize the alternatives appropriate for sheet and tubing devices.

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[35] View case studies at the Healthcare Without Harm website: www.noharm.org

Sheet Devices

The type of material used for sheet devices is dependent upon the material being stored. There are four broad groups of medical solutions that are packaged in bags:

1. Blood products (whole blood, red blood cells, platelets and fresh frozen plasma)
2. Intravenous (IV) solutions
3. Total parenteral nutrition (TPN) and enteral feeding products
4. Medications

Table 7.4.2 D summarizes the general categorization of materials that are acceptable for these packaged groups.

Table 7.4.2 D: Packaged Medical Solution and Storage Material Alternatives

Medical Solution Product	Storage Materials
Blood – Red Blood Cells	DEHP/PVC, BTHC/PVC
Blood – Platelets	DEHP/PVC, Polyolefin, Polyolefin laminated PVC
Blood – Fresh Frozen Plasma	DEHP/PVC, Polyolefin, Polyolefin laminated PVC
IV Solutions	DEHP/PVC, Polyolefin, Polyolefin laminated PVC
TPN and Enteral Feeding Products	DEHP/PVC, EVA, EVA/Polyolefin laminate
Medications	Polyolefin, Polyolefin laminated PVC

The primary products derived from whole blood are red blood cells, plasma, and platelets. Whole blood, the unseparated blood that comes from a donor, is typically stored in DEHP/PVC bags. Using a centrifuge, whole blood is separated into platelet-rich plasma and red blood cells.

Figure 7.4.2 E shows an example of an IV bag made from a polyolefin sheet material that is commercially available. When evaluating alternative materials for sheeting in the medical device industry, the ability of the sheet or film to provide a barrier to gas exchanges between the stored solution and the surrounding environment is important. Specifically, for the storage of sensitive solutions such as blood and platelets, minimizing the gas exchange of carbon dioxide and oxygen will result in a longer shelf life for the solution. Shelf-life is a critical factor driving material selection for packaging blood products because a container with a longer shelf-life reduces product losses. Other performance criteria discussed in Section 7.4 (with the obvious exception of PVC compatibility) also apply when evaluating material alternatives.

Figure 7.4.2 E: Typical Polyolefin Intravenous Bag

(Cryovac Medical, Sealed Air Corporation)

Ethylene Vinyl Acetate (EVA)

EVA is a copolymer blend of vinyl acetate, ethylene, and ethyl acetate and may contain other compounds in trace amounts. EVA has been used for medical sheet (or film) applications for parenteral and enteral solutions for many years. Empty EVA bags are also used for custom mixing of drugs by pharmacies, and because bags for these uses do not need to be steam sterilized, the temperature resistance capabilities of flexible PVC are not required.

The EHS characteristics of EVA are summarized in Table 7.4.2 E.

Table 7.4.2 E: Ethylene Vinyl Acetate Considerations

Life Cycle Phase	Environment and Human Health Issues	Positive Aspects of EVA
Raw Materials	• Co-polymer of ethylene and vinyl acetate	• Non-chlorine
Use		• Does not leach plasticizer (none present)
End of Life	• Recycling infrastructure for EVA is largely non-existent	• No potential chlorine derivatives from combustion • Recyclable

EVA bags can be sterilized by gamma radiation or ethylene oxide (EO) without negative impact on their physical properties; because the melt temperature is below 121°C EVA cannot be autoclaved (steam sterilized) and is therefore not appropriate for use in IV solution storage. Flexible films made with EVA exhibit excellent clarity and, because they are manufactured without plasticizer, they are well suited for packaging and administration of lipophilic fluids. EVA films are also promoted as combining toughness and low-temperature sealability with impact and puncture resistance (Ellay 1997). The water vapor transmission rate from EVA film is less than that of PVC film; however, its gas exchange rate is approximately twice that of PVC film (Lipsitt 1997). EVA is thus more suited for parenteral and enteral solution and drug storage rather than blood and platelet storage.

As with PVC, EVA bags can be manufactured using radio-frequency sealing equipment that provides a highly reliable seal.

Based on our review, EVA is expected to be currently only slightly more expensive than PVC for these applications. Because the density of EVA is less than that of PVC, film manufactured using EVA can be of a smaller gauge than similar PVC film. This can lead to a cost reduction, making EVA overall a cost-competitive alternative to PVC.

Polyolefins - Polyethylene (PE) and Polypropylene (PP)

The polyelefins PE and PP are widely used compounds that are valued for their flexibility, transparency and toughness. PE is manufactured in high density and low density forms (HDPE and LDPE). PE and PP are stable and inert polymers that exhibit very high resistance to chemical attack. PE resins, for example, are almost insoluble at room temperature in all organic solvents although some absorption, softening or embrittlement may occur. LDPE is more readily impacted by exposure to chemicals than HDPE. Some chemicals such as detergents and silicone oil will cause the phenomenon known as environmental stress cracking. PE and PP are very resistant to water and water vapor, which is an advantage when storing aqueous solutions which normally require an extra overwrap layer on top of PVC.

The EHS characteristics of polyolefins are summarized in Table 7.4.2 F.

Table 7.4.2 F: Polyolefin Considerations

Life Cycle Phase	Environment and Human Health Issues	Positive Aspects of Polyolefins
Raw Materials	• Petroleum based thermoplastic	• Does not require additives to achieve desired flexibility • No chlorine
Use		• Does not leach plasticizer (none used)
End of Life		• No chlorine-related combustion products of concern • Recyclable

All oils attack polyolefins to some extent. Mineral oils will dissolve the polymer at elevated temperatures and at lower temperatures they can be absorbed causing swelling, discoloration and in the extreme, disintegration. Vegetable and animal oils do not have such a pronounced effect but some may cause environmental stress cracking to occur. The influence of oily substances on the structural integrity of polyolefins can be an issue when considering the use of these polymers in medical devices as the stored solutions are often oily or lipophilic in nature.

Metallocene polyethylene (mPE) is a modification of the PE copolymer resin that uses a metallocene catalyst to control the molecular architecture of the PE resin, allowing for very low densities and narrow molecular-weight distributions. Metallocene-catalyzed PE copolymer resins (mPE) are made with specific gravities in the range of 0.86 – 0.92. mPE has greater strength and toughness, better heat-sealing properties, greater clarity and low catalyst residues compared with conventional PE (Eastman 2006). Use of mPE allows for the storage and transportation of human plasma, bone marrow, and other biologically active materials that require extremely low temperatures, from -78° to -195°C, whereas PVC is very brittle at these very low temperatures (Esposito 1997).

The toughness of mPE resins can allow for thinner, lighter-weight films, and the lower density of the mPE films results in a higher yield than is possible with PVC, producing more film area per pound (Lipsitt 1997). This can result in a lower cost device than with PVC. mPE is an emerging material alternative for the medical device market.

PE can be made biodegradable by creating weak links in the polymer chain so that bacteria and other microorganisms can break it down.

Unlike with PVC and EVA, sealing of PE medical bag devices requires additional operating control if the radio-frequency technique is desired. This is somewhat alleviated when mPE is used.

Like PE, PPs attributes include softness, flexibility, good low temperature toughness and melt point above 121°C. A commodity production plastic, PP is relatively cost effective. Additionally, with a 30% lower density than PVC, less material is needed to provide the same level of performance; creating opportunities for down gauging products. A drawback is that PP does not radio-frequency weld (Leaversuch 1999).

PP is too brittle and stiff for sole use in medical sheet devices. All PP medical sheeting require the addition of other materials to enhance its flexibility and durability. PP IV bags, for example, made by BBraun, Hospira (formerly Abbott) and Cryovac, have all developed products that include polyethylene and/or copolyester resins. The multilayer product provides toughness, clarity and flexibility (Polin 2002).

Because the barrier properties of the multilayer PP sheet devices are significantly greater, at least one supplier (Hospira) has chosen to forego the overwrap used with other IV bag products, resulting in 40-60% less waste according to Hospira (Modern Plastics 2006).

Glass

Prior to the extensive use of plastics, glass bottles were used to store medical solutions. This can still be done. Glass bottles have certain EHS advantages over other materials, which are summarized in Table 7.4.2 G.

Table 7.4.2 G: Glass Considerations

Life Cycle Phase	Environment and Human Health Issues	Positive Aspects of Glass
Raw Materials	• Silicone sand	• No chlorine present
Use	• Potential for breakage leading to worker injury	• The most inert material available on the market today for health care
End of Life		• No chlorine-related combustion products of concern • Recyclable

Glass has a major advantage in that it has excellent clarity and is virtually impermeable. Relative impermeability of glass bottles make them potentially well suited for storage of blood and platelets. However, glass bottles require special handling and storage as they are prone to breakage. Currently, glass bottles are more commonly used in the storage of small volumes of medical; they can, however, also be used to store IV solutions.

Because they are flexible and collapsible plastic containers do not need air to replace fluid flowing from the container. Being rigid, glass bottles require air vents. The incorporation of appurtenances such as vents, as well as the overall processing techniques associated with specialty glass bottle manufacture, result in higher manufacture costs than for PVC bags. As a result, glass bottles are more expensive than DEHP/PVC.

Tubing Devices

Medical tubing devices must be formed in a variety of configurations to accommodate differing medical needs. Important specifications for medical tubing include not only OD and ID, but also wall thickness. To produce medical tubing with extremely thin walls, manufacturers force material to flow through the small orifices of processing equipment. Some medical tubing includes reinforcements made from many layers of different materials.

The materials used in flexible medical tubing have to satisfy a wide range of performance and processing criteria. They must be flexible, durable and strong with a low coefficient of friction to withstand fluid flow pressures and to facilitate flow. They must be highly resistant to chemicals and to temperature variations, not only to satisfy end-use requirements, but also to tolerate the conditions encountered in various sterilization methods. They must be biocompatible and inert in contact with blood, tissue and other body fluids/matter. Transparency is at times convenient and at other times vital in order to monitor visually or electronically the flow of contents through the tube. And in the final analysis all these properties must be delivered cost-effectively in standard extrusion or co-extrusion processing equipment.

Olefins are suitable for tubing applications. The discussion of their technical, EH&S and economic considerations are presented above and do not differ significantly for tubing applications. In addition, silicone and thermoplastic polyurethane (TPU) are assessed for medical tubing alternative materials.

It is recognized that leaching of DEHP from tubing, including nasogastric tubes is of particular concern even for short time periods, less than 24 hours (Federation of Swedish County Councils 2000). Tubes used for longer than a few days are typically made from silicone or TPU. The decision of how long to leave a tube in place is a clinical decision. A benefit of short-term duration is potentially lower rates of infection (Tcholakian and Raad 2001). A benefit of longer-term duration, for example, with nasogastric tubes used in enteral feeding is reducing the frequency of inserting the tube through the nasal cavity, which causes patient discomfort (Penrod et al. 1999).

Silicone

Silicone is a synthetic rubber that exhibits certain EHS characteristics summarized in Table 7.4.2 H.

Table 7.4.2 H: Silicone Considerations

Life Cycle Phase	Environment and Human Health Issues	Positive Aspects of Silicone
Raw Materials		• No chlorine
Use		• Does not leach plasticizers (none used)
End of Life	• Difficult to recycle	• No potential chlorine derivatives from combustion

Silicone tubing has demonstrated superior performance properties that make it well suited for medical device applications. Silicone is naturally translucent (though not entirely clear), odorless and tasteless. Silicone is biologically inert and its inherent lubricity and flexibility eases medical procedures.

Conventional silicone elastomers can have fairly high ultimate elongations, but only low-to-moderate tensile strengths. Consequently, the toughness of most biomedical silicone elastomers is not particularly high. One of the least attractive properties of conventional silicone elastomers in device manufacturing is that the materials require covalent cross-linking to develop useful properties. Fabrication of device components must include, or be followed by, cross-linking to form chemical bonds among adjacent polymer chains. Cross-linking of extrudable and moldable silicone stock is usually done via peroxide-generated free radicals adding to vinyl groups incorporated along the polymer backbone, or, increasingly, by the platinum-catalyzed addition of silane.

Regardless of how the cross-linking is accomplished, the resulting thermoset silicone cannot be redissolved or remelted. This reduces the number of post-fabrication operations that can be used in device manufacturing with these silicones. For instance, thermal forming, tipping, and tapering; radio-frequency welding; heat sealing; and solvent bonding are all useful post-fabrication methods that are essentially unavailable when building devices from conventional silicone (Ward 2000).

Cost information for silicone tubing was obtained from one industry source at a range of $90 - $110/100 linear feet of tubing. This is a snap-shot cost estimate that can be compared to the same source's estimate of cost for PVC tubing at $40 - $45/100 linear feet of tubing for similar gauge. The cost per linear foot provides a very rough gauge of the cost per treatment because silicone products are used for longer term applications than DEHP/PVC. For example, the cost of providing 30 days of feeding through a nasogastric tube will depend on the number of tubes used. Since DEHP/PVC, with its shorter use life, will require more tubes (than silicone), the comparative cost of silicone relative to DEHP/PVC for functional unit will decline relative to the comparative per pound price. No studies were located detailing the cost differences per treatment period.

Tubing that remains in the body for days as part of the medical procedure is usually made from silicone or TPU because these materials do not turn brittle over time, as does PVC tubing (a characteristic that may be associated with migration and loss of plasticizer from the polymer matrix into the body). However, studies indicate that infection can be associated with the use of silicone tubing in uses such as parenteral feeding, and that the infection can begin almost immediately (Tcholakian and Raad 2001). Silicone can however withstand repeated sterilization. One study evaluated the level of residual EO present in three medical grade tubing materials (PVC, silicone and TPU) after sterilization. The absorption and desorption of EO from PVC and TPU tubing were similar. In contrast, silicone tubing absorbed 85% less EO. The time required for desorption of residual ethylene oxide was 2 hours for silicone tubing and 7 to 8 hours for PVC and TPU tubing (McGunnigle et al. 1975).

Thermoplastic Polyurethane (TPU)

In contrast to cross-linked silicone, many polyurethane elastomers are thermoplastic in nature. Specifically, TPU elastomers can be processed by methods that involve melting or dissolving the polymer to reshape it. The molecular structure of a typical biomedical TPU consists of alternating high-melting "hard" urethane segments and liquid-like "soft" segments.

Cost information for TPU tubing was obtained from one industry source at a range of $110 – 120 / 100 ft of tubing. This is a snap-shot cost estimate that can be compared to the same source's estimate of cost for PVC tubing at $40 - $45/100 ft of tubing. The cost per linear foot provides a very rough gauge of the cost per treatment because TPU products, like silicone, are used for longer term applications than DEHP/PVC. Since DEHP/PVC, with its shorter use life, will require more tubes (than TPU), the comparative cost of TPU for functional unit will decline relative to the comparative per pound price. No studies were located detailing the cost differences per treatment period.

TPU is formed by reacting an alcohol containing more than two reactive hydroxyl groups per molecule with a diisocyanate or a polymeric isocyanate in the presence of suitable catalysts and additives. The primary diisocyanates used in the manufacture of TPU are methylene diphenylene diisocyanate (MDI) and toluene diisocyanate (TDI).

Both MDI and TDI are regulated based on their environmental and human health impacts and are listed on the Massachusetts Science Advisory Board's list of more hazardous chemicals. The production of TPU has been linked to numerous occupational health problems including heart disease, asthma, and reduced sperm quality. In addition, incineration of TPU releases numerous hazardous chemicals including isocyanates and hydrogen cyanide. Polyurethanes are also potentially more hazardous in the work environment than PVC (Tickner 2000).

The EHS considerations associated with TPU are summarized in Table 7.4.2 I.

Table 7.4.2 I: Thermoplastic Polyurethane Considerations

Life Cycle Phase	Environment and Human Health Issues	Positive Aspects of TPU
Raw Materials	• MDI and TDI used in manufacture or TPU – associated occupational exposure hazards	• No chlorine in final product
Use		• Does not leach plasticizer (none used)

Table 7.4.2 I: Thermoplastic Polyurethane Considerations

Life Cycle Phase	Environment and Human Health Issues	Positive Aspects of TPU
End of Life		• Can be mechanically or chemically recycled • No potential chlorine derivatives from combustion

Conventional TPU generally has excellent physical properties, combining high elongation and high tensile strength to form tough elastomers. Whereas natural rubber latex may have an initial modulus of a few hundred pounds per square inch (psi), an 80A aromatic TPU might have a modulus of >2000 psi, making it considerably less compliant. Aromatic polyether TPU, on the other hand, can have excellent flex life, a tensile strength of >5000 psi (34 MPa), and ultimate elongations of >700% (Ward 2000).

Summary of Material Alternatives Assessed for Medical Devices

Based on the discussion presented above, the following table summarizes the key assessment criteria for sheet and tubing medical devices as compared to DEHP plasticized PVC.

Table 7.4.2 J: Materials Alternatives Assessment Summary for Medical Devices

Key Assessment Criteria		DEHP/PVC Reference	Comparison of Materials to DEHP/PVC				
			EVA	Polyolefin	Glass	Silicone	TPU
Performance	Elastic Recovery	**Excellent**	?	=	-	=	-
	Cold Flexibility	**Good**	?	?	-	+	=
	Sterilizability (Radiation, Ethylene Oxide, Steam)	**Good** (R, EO, S)	= (R, EO) - (S)	= (R, EO) - (S)	=	=	=
	Gas Permeability	**130** cm^3-mm/m^2/day	-	-	=	?	?
	Manufacturability	**Good**	-	=	+	-	-
Cost	Raw material cost (Sheet)	**~\$25**/ft^2	=	=	-	NA	NA
	Raw material cost (Tubing)	**~\$45**/100ft	NA	=	NA	-	-
	Relative Use Cost (Tubing)[36]	**~\$45**/100ft	NA	=	NA	?	?

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[36] This cost factor assumes the relative use life of tubing, with DEHP/PVC and polyolefin assumed to be limited to short term use in applications such as enteral feeding (requiring multiple insertions of new tubing), and silicone and TPU assumed to be appropriate for longer term use of a single tubing set in similar applications. The ? for silicone and TPU indicates that the actual use cost relative to DEHP/PVC is not known, and is related to the number of new tubing sets required per procedure.

Key Assessment Criteria		DEHP/PVC Reference	Comparison of Materials to DEHP/PVC				
			EVA	Polyolefin	Glass	Silicone	TPU
Environmental Criteria	Derived from Sustainable Material	**No**	=	=	+	=	=
	Recyclable[37]	**Possible**	-	=	+	-	=
	End of Life	**Potential Hazardous Byproduct Generation** (Incineration)	+	+	+	+	+
Human Health	Human Exposure to Chemicals During Use	**Leaching of plasticizer**	+	+	+	+	+

Comparison Key + Better = Similar - Worse ? Unknown **NA** not applicable/not assessed

7.4.3 Alternatives Assessment for Wall Coverings

DEHP/PVC wall coverings are used in both commercial and residential settings for decorative as well as protective purposes. Vinyl wall coverings are popular because they are available in a wide array of different patterns and colors and are both durable and scrubbable. DEHP is not the only plasticizer used in vinyl wall covering applications. Most vinyl wall covering products sold in the European Union do not contain DEHP. Because of market drivers, nearly all vinyl wall covering sold in the United States today is made in China and Southeast Asia. According to industry sources, the majority of US vinyl wall covering imports use DEHP (Eastman 2006). Commercial wall coverings are available in 54 in. widths in 30 or 50-yard roll lengths and residential are made into 20.5 in. to 28 in. widths (VBD 2006).

Composition

The exact formulation of most vinyl wall coverings varies among manufacturers, who keep their chemical compositions proprietary. Additives typically used in most products include:

1. Plasticizers to improve low temperature product flexibility, and stain and abrasion resistance, and can impact fire retardancy.
2. Stabilizers to prevent the vinyl from degrading during high temperature processing and prevent discoloration of the finished product.
3. Other additives including pigments, fungicides, flame-retardants or smoke suppressors (VBD 2006).

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[37] For medical devices that are considered a biohazard recycling is only appropriate when specially managed (*e.g.,* steam sterilized prior to recycle), which may limit the opportunity for recycling as a management method.

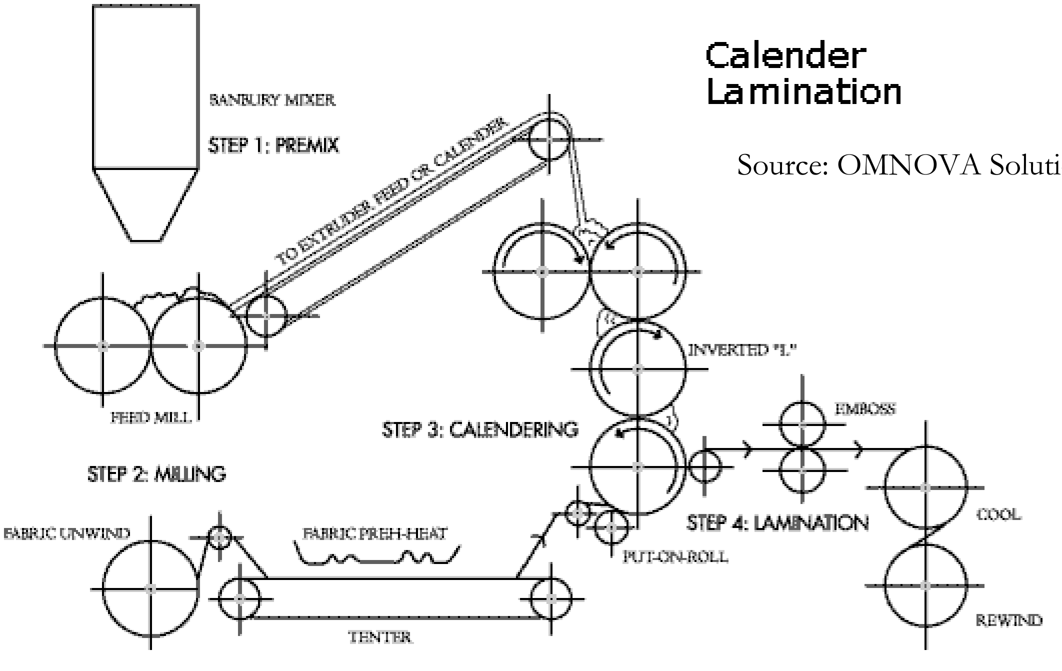
Vinyl Wall Covering Production

The production of vinyl wall coverings includes mixing and calendaring, printing, embossing and texturing and finishing. A process called "calendaring" is often the initial stage of vinyl wall covering production (see Figure 7.4.3 A) Calendaring begins by mixing and heating several ingredients (including PVC, stabilizers and plasticizers) to a uniform consistency. The compound is heated and "squeezed" through a series of hot metal rollers that flatten the vinyl compound into a sheet of vinyl film. The process is repeated until the film reaches a specific uniform thickness. During the final stage of the calendaring process, a fabric backing can be added to the film using a mixture of heat and pressure. Wall coverings can also be produced using a pre-mixed liquid vinyl called plastisol and a manufacturing technique similar to the calendaring process.

Finishing operations such as printing, embossing, and texturizing follow the calendaring or plastisols production process. During this stage of the manufacturing process, large, specialized printing presses apply one or more stages of ink to the vinyl surface to create specific wall covering colors and patterns. A surface texture can also be applied to the wall covering using embossing rollers.

The final stage of production includes applying a finish or top coating to the surface of the wall covering. These coatings include a basic clear vinyl coating or a clear film laminate to provide additional surface protection, durability and cleanability (OMNOVA Solutions 2006).

Figure 7.4.3 A: The Calendering Process



Calender Lamination

Source: OMNOVA Solutions

Installation/Cleaning/Maintenance

Surface preparation, such as making sure that the wall surface is clean, dry, structurally sound and free of grease, mildew or other stains, ensures that the wall covering permanently adheres to wall surfaces. Selecting the correct adhesive and surface treatment is also essential when installing vinyl wall covering. Many manufacturers recommend professional installation to ensure long life.

Manufacturers recommend cleaning with a mild detergent to remove accumulated dirt, grease and most stains without damaging the vinyl wall coverings. Stains should be removed as soon as possible. Ordinary dirt spots can be removed with a mild soap and warm water. Rinse thoroughly with clean water. For more difficult stains that are only surface deep, manufacturers recommend a stronger detergent.

Financial

Typically, the installation cost for vinyl wall covering, including equipment and labor, ranges between $7.00 to $10.00 per linear yard, depending on the thickness and pattern. Uninstalled retail vinyl wall covering costs range anywhere between $3.00 and $5.00 per linear yard for low end product up to between $14.00 and$22.00 per linear yard for high end product. Higher quality vinyl wall covering is thicker and is expected to last for more than 25 years (Vinyl Institute 2006).

Environmental and Human Health Issues

The principal environmental and human health issues associated with DEHP/PVC wall covering are similar to those of DEHP/PVC flooring. Table 7.4.1B outlines these issues in detail, examining PVC intermediates manufacturing, human health impacts of DEHP, and the potential for chlorine related emissions from uncontrolled or poorly controlled PVC incineration[38]. Other impacts include energy use impacts from manufacturing and transport and a lack of end-of-life recycling and recovery options.

Specific Plasticizer Alternatives for Wall Coverings

In the initial prioritization DEHA and DINP were found to be feasible alternatives. Wall covering manufacturers have suggested that DINP may be acceptable as a 'drop in' replacement which off-sets its higher raw material cost (Carnegie 2006).

Di Ethylhexyl Adipate (DEHA)

DEHA is an adipate plasticizer whose specific chemical structure is shown in Figure 7.4.1F. Adipates have a different chemical structure from phthalates, with the synthesis of the first based on adipic acid as opposed to the synthesis of the second, which is based on phthalic anhydride. The adipates are classified as low temperature plasticizers and are all relatively sensitive to water (*DEPA 2001*). The volatility of DEHA is lower than DEHP, with a vapor pressure of 8.5 x10^{-7} mmHg (refer to Appendix C for data). DEHA is also less compatible with PVC (than DEHP), which can lead to exudation (*i.e.,* plasticizer migrating to the surface), causing an undesirable appearance on the surface of the PVC. DEHA is known to be slightly more difficult to process compared to DEHP.

The Danish EPA conducted a review of toxicological data associated with a number of plasticizers, including DEHA. A NOAEL of 610 mg/kg bw/day has been reported (DEPA 2001), which is orders of magnitude higher (*i.e.,* indicating lower toxicity) than the NOAEL for DEHP. The Chronic Health Advisory Panel for the US Consumer Product Safety Commission quotes a study that indicates a fetotoxicity issue associated with oral exposure to DEHA (CHAP 2001).

Diisononyl Phthalate (DINP)

DINP is a phthalate ester plasticizer made from C9 alcohols as opposed to C8 alcohols used in the manufacture of DEHP. The chemical structure of DINP is depicted in Figure 7.4.1B. The plasticizing efficiency of DINP is somewhat lower than DEHP and therefore more plasticizer is required to gain the same softness. Because the molecular weight of DINP (418) is greater than DEHP (390), DINP has better high temperature performance and extraction resistance. Compared

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[38] For a more detailed outline of DEHP/PVC environment and human health issues, readers are encouraged to review the US Green Building Council website on PVC: http://www.usgbc.org/DisplayPage.aspx?CMSPageID=153).

with DEHP, DINP processing emits noticeably lower levels of plasticizer mist from process equipment. As a result, there is less plasticizer lost to the air and more retained in the product, therefore overall cost savings.

DINP is a "drop in replacement" for DEHP. To process well, plasticizers must be absorbed into the PVC resin particles during this blending process (DEPA 2003). Known as processability, PVC resin, plasticizer(s), stabilizers and lubricants should blend together readily in a high-speed mixer or a ribbon blender. DINP's processability is similar to DEHP's.

Exposure to DINP during processing or use of wall coverings is expected to be minimal due to the lower emissions relative to DEHP. During use there is little likelihood that DINP will migrate out of the polymer matrix and be exposed to humans. In the event that humans do become exposed to DINP from this use however, there may be associated health effects.

According to the Chronic Health Advisory Panel, exposure to DINP results in potential acute toxic effects (CHAP 2001). The NOAEL for systemic toxic effects induced in laboratory animals by exposure to DINP is estimated to be between 15 mg kg/d and 88 mg/kg bodyweight/d. To put this into context, a study by the Consumer Council Austrian Standards Institute (Fiala n.d.) used the lowest NOAELs for DINP and DEHP to determine a total daily intake level for these plasticizers (this study focused on the use of DINP and DEHP in children's toys that would be mouthed, using a safety factor of 100) of 15.0 μg/kg bodyweight /d for DINP and 37 μg/kg bodyweight /d for DEHP.

According to its review of relevant studies, the CHAP concludes that DINP is clearly carcinogenic to rodents, inducing hepatocellular carcinoma in rats and mice of both sexes, renal tubular carcinoma in male rats, and mononuclear cell leukemia in male and female rats. The studies they reviewed also suggest possible carcinogenicity in the testis, uterus, and pancreas (CHAP 2001). DINP has not been listed as an EPA or IARC possible human carcinogen.

Summary of Plasticizer Alternatives for DEHP

The primary plasticizer alternatives for DEHP vinyl wall covering include a phthalate plasticizer, DINP and an adipate plasticizer, DEHA. While DINP had a higher cost premium than desired, information from plasticizer as well as wall covering manufacturers indicated that DINP should be further examined. DEHA met all of our preferred attributes including cost, performance and environmental health and safety. The two plasticizers were compared to DEHP for all criteria; the results are shown in Table 7.4.3 A.

Table 7.4.3 A: Summary of Plasticizer Alternatives Assessment for Wall Covering

Assessment Criteria		**DEHP (Reference)**	**Comparison Relative to DEHP**	
			DEHA	**DINP**
Technical/ Performance Criteria	Volatility	**1.4 x 10-6 mm Hg**	+	=
	Compounding	**Good**	=	=
	Tensile Elongation (life of product)	**MW 390**	=	=
	PVC Compatibility	**Good**	-	=
	Emissions • Manufacture • Use	**Acceptable (M, U)**	-	=
Cost	Cost /lb applied	**$0.70** (March 2006)	=	=
Environmental Criteria	Persistence	**Sediment (140 days)**	+	=
	Bioaccumulation	**BCF = 320**	+ (BCF = 61)	+ (BCF = 3.2)
	Aquatic (Fish) Toxicity	**>0.0025 mg/L**	+ (>100 mg/L)	= (>0.14 mg/L)
Human Health Criteria	Carcinogen	**EPA B2, IARC 3**	?	= (indicated in rodents – *CHAP 2001*)
	Reproductive Toxicity	**Yes** **(Prop 65, EU; NOAEL = 3.7 – 100 mg/kg bw/d)**	= (potential fetotoxicity, NOAEL = 610)	+
	LD50	**34 g/kg**	- (5.6 g/kg)	?
	Irritation	**Yes** (Dermal, Ocular, Respiratory)	+ (D) = (O,R)	+

Comparison Key + Better = Similar - Worse ? Unknown

Material Alternatives Analysis

This section analyzes three priority alternative materials: Glass Woven Textiles, Cellulose/ Polyester Blends, and Wood Fiber/Polyester Blends.

Wall Covering Material Alternative #1: Glass Woven Textiles

Glass woven textile wall coverings are manufactured in the U.S. by Johns Manville (JM) and known by the trade name Textra™. The wall coverings include recycled glass and gypsum. Glass textile wall coverings have been used in Europe for more than 60 years and are mandatory for government and health care facilities in Germany (Glass Textile North America (GTNA) 2005). These wall coverings can be painted and re-painted up to 8 times to change the decor. JM offers more than 20 patterns and estimates a product lifetime of more than 30 years. Both scrubbable and durable, these wall coverings are breathable, reducing the chance of mold and/or mildew.

Construction

According to the manufacturer, the composition of this material is as described in Table 7.4.3 B.

Table 7.4.3 B: Composition of Glass Woven Textiles

Wt. %	Material	Origin/Precursor Materials
>60%	Continuous filament glass fibers	Sand
<40%	Binder	Starch, cellulose derivative and polymer

Installation/Cleaning/Maintenance

Regular maintenance of the woven textile wall covering includes dusting with a dry mop. If there are marks on the wall, they can be scrubbed with a wet cloth. Remove, patch and paint damaged sections. The wall covering can also be repainted to clean it up or change the look of a room. Detailed installation instructions are available at www.jm.com.

Financial

Installation equipment and labor cost for Textra™ wall covering ranges from $7 to $10 per linear yard, depending on the contractor and equipment costs. Textra™ glass woven textile wall coverings cost between $13.00 and $15.00 per linear yard depending on the pattern. The total costs for Textra™ wall coverings are between $20 and $35 per linear yard when professionally installed.

Environmental and Human Health Issues

Textra™ wall covering products meet State of Washington and USEPA indoor air pollution criteria for particles, VOCs and formaldehyde. Glass woven textiles are made from natural ingredients; sand to make the glass and some potato based starch to increase stiffness and make it easier to hang. The glass manufacturing process is very energy intensive. Very high temperatures are required to melt sand and make glass. The fuel burned to reach the high temperatures produces NO_x, an ozone precursor, and CO_2, a greenhouse gas. A water-based latex adhesive is recommended for installation. There are VOC emissions upon installation and when the product is painted. Low VOC paint is widely available and can be used to reduce these emissions. At the end of life, glass woven textile wall coverings are most commonly left in place to strengthen the wall. When left in place, there is no need to dispose of the old product until the building is dismantled.

Table 7.4.3 C: Glass Woven Textiles Considerations

Life Cycle Phase	Environment and Human Health Issues	Positive Aspects of Glass Woven Textiles
Raw Materials	• Natural ingredients sustainable • Minimal recycled content; only includes 5% postindustrial glass from manufacturing process	• Derived from natural ingredients (sand and potato based starch)
Manufacture	• Energy use and associated greenhouse gas, particulate and other related emissions • NOx generation during the manufacturing process	
Installation	• Surface topcoat of paint primer usually applied • If painted after installation, high VOC paints will cause emissions	• Latex based (VOC free) clear adhesive recommended for installation • Can use low VOC paint and primer on wall covering
Use and Maintenance	• Re-painting recommended to remove stubborn stains • Patch damaged sections, or change décor • VOC emissions can result	• Dusting with a dry mop for regular cleaning
End of Life	• Not recyclable or compostable • If removed, product is landfilled	• Leaving the product in place to strengthen the wall at the end of life • Re-covering with new wall covering is common • No chlorine products generated if incinerated

Wall Covering Material Alternative #2 – Wood Fiber/Polyester

Wood Fiber and polyester wall covering, specifically the Allegory™ series from Innovations in Wall Coverings (IWC), is made of 50% virgin spun-woven polyester and 50% wood fiber and comes in 34 different colors. Washable, scrubbable and stain resistant, the wall covering breathes and therefore reduces mold and mildew formation. It does not require backing and adheres directly to wall surfaces.

Installation/Cleaning/Maintenance

Professional installers report that Allegory™ wall coverings hang easier than standard vinyl wall coverings because it is lighter and easier to maneuver. Manufacturers of the wood fiber /polyester wall covering recommend using a qualified installer to apply the wall covering. While the use of a clear strippable adhesive is recommended, they do not recommend any specific brand.

To remove dirt and smudges, a mild soap and warm water solution followed by a rinse with clean clear water and a soft cloth is recommended. Only soft bristle brushes are advised. Damp spots and stains should be treated promptly to ease clean-up. Blotting with an absorbent cloth or polyester sponge is recommended.

Financial

Installation cost, including equipment and labor for wood fiber/ polyester wall covering ranges from $7 to $10 per linear yard, depending on the contractor and equipment costs. Allegory™ wood fiber/polyester wall covering costs $14.95 per linear yard (as of 3/06) and is backed by a one year warranty.

Environmental and Human Health Issues

Allegory™ is made using wood pulp from managed forests. The forests are certified using the European Sustainable Forestry Initiative (SFI). SFI was developed in 1995, and is described as "raising the floor of minimum standards of forest management and aims to improve the image of US forest products industry (Canadian Environmental Network 2006)." Allegory™ is heavy-metal free and contains water soluble inks. Allegory™ contains no recycled content. IWC claims the Allegory™ product can be recycled, although this may be difficult given the mixed plastic-wood fiber material. Furthermore, no formal take-back program has been established.

Table 7.4.3 D: Wood Fiber/Polyester Considerations

Life Cycle Phase	Environment and Human Health Issues	Positive Aspects of Wood Fiber/Polyester Wall Covering
Raw Materials	• Mix of wood pulp and spun woven polyester. Does not contain recycled content.	Wood pulp from managed SFI forests.
Manufacture	• Energy use and associated greenhouse gas, particulate and other related emissions. VOC generation during the manufacturing process.	
Installation	• Off-gassing of adhesives	
Use and Maintenance	• Cleaning, VOC off gassing potential depending on product used.	Can be cleaned with a mild detergent
End of Life	• No take-back program • Recycling may be difficult due to mixed plastic-wood fiber material.	• Product is recyclable • No chlorine products generated if incinerated

Wall Covering Material Alternative #3 - Cellulose/ Polyester Blend

Cellulose/polyester blend wall coverings are sold under a few brand names (Enspire™ and EnVision™) and are expected to last between 10 and 15 years. These non-woven blends are breathable, reducing the risk of mold and mildew growth. The wall coverings are scrubbable and available in over 40 colors and patterns colors and patterns.

Table 7.4.3 E: Cellulose/Polyester Wall Coverings

Manufacturer	Trade Name	Construction
MDC Wallcoverings	Enspire™	Polyester/cellulose
NaturDecor & Supply	EnVision™	Nonwoven polyester-cellulose blend
Seabrook Contract	Nonwoven Wall Materials	70% polyester 30% cellulose

Installation/Cleaning/Maintenance

The manufacturers of these wall coverings recommend professional installation. The wall surface must be cleaned and dried before installation. Detailed installation instructions are available at www.mdcwallcovering.com.

For maintenance purposes, stains should be removed immediately with a clean sponge or cloth. The material can be rinsed with water if necessary. For cleaning, use a soft detergent (e.g. dishwashing detergent) if necessary and then rinse with water. Hard rubbing and excess water should be avoided.

Financial

Installation costs for cellulose and polyester wall covering range from $7 to $10 per linear yard, depending on the contractor and equipment costs. Enspire™ wall covering costs between $18 and $22 per linear yard depending on the pattern.

Environmental and Human Health Issues

The Enspire™ collection by MDC Wallcoverings can be returned using the Ecologic Reclamation Program run by the manufacturer. This program, which claims to be the first of its kind in the wall covering industry, has succeeded in finding a variety of secondary uses for old wall covering. It provides the opportunity to specify environmentally friendly materials that would otherwise end up in landfills. There are specific requirements for the reclamation program that can be found on MDC Wallcoverings web site; www.mdcwallcoverings.com.

Enspire™ is PVC- and chorine-free, and the cellulose is from totally chlorine free (TCF)-pulp. The wall covering is made using water-based inks that contain no heavy metals and are formaldehyde free. Polyester is defined as a "long-chain polymers chemically composed of at least 85% by weight of an ester and a di-hydric alcohol and a terephthalic alcohol." Two types of polyester are commercially manufactured today are polyethelene terphthalate (PET) and poly-1,4 cyclohexylene dimethylene (SwicoFIL AG Textiles 2006).

An important additional consideration associated with these cellulose/polyester blends is the use of Teflon® coatings. These coatings are routinely applied to provide improved stain resistance and washability. However the use of Teflon® indicates a potential occupational exposure issue associated with the perfluorinated compounds from which Teflon® is manufactured. An assessment of the impact of this potential is beyond the scope of this study, but it should be noted.

Table 7.4.3 F: Cellulose/ Polyester Considerations

Life Cycle Phase	Environment and Human Health Issues	Positive Aspects of Cellulose/ Polyester Wall Covering
Raw Materials	• Mix of polyester and cellulose. Sustainability of natural ingredients (e.g. cellulose) not assured. No recycled content	
Manufacture	• Energy use and associated greenhouse gas, particulate and other related emissions • VOC generation during the manufacturing process. • Surface topcoat of Teflon® often applied	
Installation	• Some adhesive offgas VOCs	• Can use "natural" adhesives based on wheat and corn starch polymers
Use and Maintenance	• Cleaning VOC off gassing potential	• Can be cleaned with a mild detergent
End of Life	• Not recyclable • Secondary Uses?	• Ecologic reclamation program run by MDC wall coverings will take back the old product • No chlorine products generated if incinerated

Wall Covering Material Alternative #4 – Wood Pulp/Recycled Paper

The wood pulp/recycled paper wall covering the Institute studied is sold by Designtex under the brand name Duraprene™. Duraprene™ is composed of wood pulp from sustainable managed forests and recycled paper and board[39]. Designtex manufactures the wall covering using wood pulp mixed with latex and sealed with a water-based polyurethane coating, providing a scrubbable and durable surface. The 20 colors used in the 11 current patterns are absorbed by the paper so they will not lift off with cleaning. Table 7.4.3 G details the construction of Duraprene™ wood pulp/recycled paper wall covering.

Table 7.4.3 G: Wood Pulp/ Recycled Paper Wall Covering

Manufacturer	Trade Name	Construction
Designtex	Duraprene™	• 50% wood pulp (cellulose) • 40% post-industrial waste • 10% post consumer recycled waste • Sealed with water-based polyurethane coating

Installation/Cleaning/Maintenance

The manufacturer recommends checking for moisture problems before installing any wall covering. Moisture could have an effect on mold and mildew growth after wall covering installation. Before beginning installation, make sure that the surface is clean, smooth, dry and structurally intact. A clay-based or "clear" vinyl adhesive and primer by the same manufacturer is recommended[40].

The manufacturer recommends routine maintenance including regular vacuuming and promptly treating spots and stains. Excessive rubbing and brushing can cause fuzzing and should be avoided (Designtex 2006).

Financial

Installation cost for the Duraprene™ wall covering range from $7 to $10 per yard, depending on the contractor and equipment costs. Duraprene™ wall covering costs between $18 and $20 per yard depending on the pattern.

Environmental and Human Health Issues

Duraprene™ uses recycled office paper and salvage from carton manufacturing and wood pulp. Duraprene™'s recycled content is reported to be 6% post-consumer and 28% total recycled composition.

Table 7.4.3 H: Wood Pulp/Recycled Paper Considerations

Life Cycle Phase	Environment and Human Health Issues	Positive Aspects of Wood Pulp /Recycled Paper Wall Covering
Raw Materials	Sustainability of natural ingredients not assured	• Contains post-consumer recycled materials. • Up to 28% recycled composition
Manufacture	Wood pulp mixed with latex	• No Teflon® topcoat applied
Installation		• Sealed with water-based polyurethane

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[39] Despite several calls to the manufacturer, we were unable to find out the specific forest certification scheme used.

[40] Detailed installation instruction can be found at: www.dtex.com/files/durapreneHanging.pdf.

Table 7.4.3 H: Wood Pulp/Recycled Paper Considerations

Life Cycle Phase	Environment and Human Health Issues	Positive Aspects of Wood Pulp /Recycled Paper Wall Covering
Use and Maintenance	Avoid excessive rubbing and brushing can cause fuzzing	• Can be cleaned with a mild detergent
End of Life	Compostable but no infrastructure	• Biodegradable raw materials • Compostable but no infrastructure • No chlorine products generated if incinerated

Wall Covering Material Alternative #5 – BioFibers

BioFiber or natural textile wall coverings are made from a variety of natural materials from cotton and linen to wood pulp and viscose. They are usually laminated to a backing to make the product more stable and to prevent the adhesive from coming through to the surface. These backings are usually paper or acrylic. Natural textiles can be finely designed or coarse in texture depending on the desired look.

Construction

MDC Wallcoverings Naturals line includes wall coverings made from a variety of different natural materials including cotton, viscose, wood pulp, sisal, and linen. Viscose is a natural polymer made from wood pulp, also known as rayon. Sisal is a natural fiber extracted from the long leaves of sisal plants. The specific products available in the line are outlined in Table 7.4.3 I below. These are paper backed, Teflon® treated products. The Teflon® treatment ensures durability and makes the product suitable for commercial applications.

Table 7.4.3 I: MDC Wallcoverings Natural Line of BioFibers

Product Name	Type	Cotton	Viscose	Wood-pulp	Linen	Sisal	Polyester	Poly-propylene
Belize and Bargello	Textile	40%	60%					
Carina	Textile	10%	75%				15%	
Casablanca	Textile	50%	50%					
Leoni/Cavalli	Textile	20%	40%				20%	20%
L – Torrens	Textile	40%	30%		30%			
L – Logan, Devonport and Camberra and L Naturals IV - Hobart	Textile				100%			
L – Brisbane	Textile	20%			80%			
L- Lismore	Textile	95%					5%	
L – Wales	Textile	35%			65%			
L Naturals III - Hirano and Emilla	Textile	20%			80%			
L Naturals III - Callisto	Textile	40%			60%			
Loft and Papasan	Suede						100%	
Sohi	Textile	40%	40%				20%	
Theda	Textile	20%	50%				30%	
Filament	non-woven			30%			70%	
Gossamer	non-woven			40%		10%	50%	
Labyrinth	non-woven						100%	

Installation/Cleaning/Maintenance

The manufacturer recommends professional installation of the Naturals Wallcovering line. Specific installation instructions including surface preparation, adhesive application, and material hanging can be found on the MDC Wallcoverings website www.mdcwall.com.

For general maintenance, light brushing or occasional vacuuming is recommended. Stains should be treated immediately usually with a moist cloth. Tougher stains should be treated with a weak detergent solution.

Financial

Cost information for these products was not available at the time of this report preparation.

Environmental and Human Health Issues

BioFiber wall covering products are made from natural fibers and are paper backed, making them both renewable (less than 10 years) and recyclable. They also release minimal indoor air pollutants such as VOCs. An important additional consideration associated with many of these biofiber blends is the use of Teflon® coatings. These coatings are routinely applied to provide improved stain resistance and washability. However the use of Teflon® indicates a potential occupational exposure issue associated with the perfluorinated compounds from which Teflon® is manufactured. An assessment of the impact of this potential is beyond the scope of this study, but it should be noted.

Viscose (rayon) was the first manufactured fiber, but unlike most man-made fibers, it is not synthetic. It is made from wood pulp and as a result, its properties are more like natural cellulosic fibers (e.g. cotton or linen) than the thermoplastic, petroleum-based synthetic fibers (e.g. nylon or polypropylene). Viscose is made using two different chemical and manufacturing techniques to develop two types of rayon, viscose rayon and cuprammonium[41].

The polyester manufacturing process is described in the Alternative #3 - Cellulose/ Polyester section. Linen (also known as flax) fiber comes from the stalk of a *Linum usitatissimum* plant. France is the world's top flax producer. 70% of linen is composed of cellulose.

Table 7.4.3 J: BioFiber Considerations

Life Cycle Phase	Environment and Human Health Issues	Positive Aspects of Natural Wall Coverings
Raw Materials	• Sustainability of natural ingredients not assured • Does not contain recycled content. • Manufactured in Europe (linen) • Conventional cotton known to be herbicide and pesticide intensive	• Derived from natural ingredients
Manufacture	• Processing (viscose and polyester) requires high water and energy use resulting in air emissions and water pollution • Surface topcoat of Teflon® applied	
Installation	• Premixed vinyl clear adhesive could off gas VOCs	• Can use adhesive based on natural polymers (e.g. wheat, and corn starch)
Use and Maintenance		• Can be cleaned with water or a mild detergent

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[41] http://www.swicofil.com/products/200viscose.html

Table 7.4.3 J: BioFiber Considerations

Life Cycle Phase	Environment and Human Health Issues	Positive Aspects of Natural Wall Coverings
End of Life		• Paper backed, makes them renewable and recyclable • No chlorine products generated if incinerated

Wall Covering Material Alternative #6 - Polyolefin

Polyolefin/ synthetic textile wall coverings are woven and non-woven looking wall coverings that were developed to give the appearance of a natural textile while adding better stain resistance and durability. These products generally have an acrylic or paper backing. Many of these products are made of polyolefin yarns, which are olefin fibers made from polymers or copolymers of propylene.

Construction

MDC Wallcoverings has a line of polyolefin wall coverings. There are 18 different colors/patterns available. This line is made of woven polyolefins that are known to be good for high traffic areas. This is due to their stain and abrasion resistance. These wall coverings have a Teflon® treated finish, which enhanced their durability. In this collection, the fibers are solution dyed which means that the color pigment is mixed into the spinning solution before extrusion. As a result the color becomes an integral part of the yarn and does not rub off or fade when vacuumed or cleaned.

Table 7.4.3 K: MDC Polyolefin Wallcoverings

Type	Backing	Finish
100% Olefin	Acrylic	Teflon® Treated
50% Olefin 50% Polyester	Acrylic	Teflon® Treated
85% Olefin, 15% Polyester	Acrylic	Teflon® Treated

Installation/Cleaning/Maintenance

The manufacturer recommends professional installation of the Polyolefin Wallcovering line. Specific installation instructions including surface preparation, adhesive application, and material hanging can be found on the MDC Wallcoverings website www.mdcwall.com.

Regular maintenance of the polyolefin wall coverings includes vacuuming and dusting with a dry cloth. Since the yarns in the polyolefin wall coverings do not absorb water, stains will remain on the surface where they can be removed with a clean, dry cloth.

Financial

Installation cost for the polyolefin wall covering ranges from $7 to $10 per yard, depending on the contractor and equipment costs. MDC Polyolefin wall covering costs between $18 and $22 per yard depending on the pattern.

Environmental and Human Health Issues

Polyolefin wall coverings are made from petroleum-based ingredients. Polyolefin wall coverings are often treated with a Teflon® finish to increase both the durability and scrubbability. The use of Teflon® indicates a potential occupational exposure issue associated with the perfluorinated compounds from which Teflon® is manufactured. An assessment of the impact of this potential is beyond the scope of this study, but it should be noted.

It is recommended that these wall coverings be installed using a premixed, heavy-duty vinyl adhesive. These adhesives are made using either natural polymers (wheat and corn starch) or synthetic polymers. Although polyolefins can be recycled there is no known take-back or recycling programs in place.

Table 7.4.3 L: Polyolefin Considerations

Life Cycle Phase	Environment and Human Health Issues	Positive Aspects of Polyolefin
Raw Materials	• Derived from petroleum based ingredients • No recycled content	
Manufacture	• Energy use and associated greenhouse gas, particulate and other related emissions. • Air pollutants generated during the manufacturing process. • Teflon® treated finish	
Installation	• Premixed, heavy-duty vinyl adhesive could off gas VOCs	• Can use a vinyl adhesive made from natural polymers
Use and Maintenance		• Can be cleaned with water or a mild detergent
End of Life	• Recycling or take back program not in place.	• Can be recycled • No chlorine products generated if incinerated

Wall Covering Materials Alternatives Summary

TURI analyzed six wall covering alternatives to DEHP-PVC. The alternatives include both natural fibers and other petrochemical derived polymers and come in a wide range of colors and patterns. Most of the alternatives are comparable in price to high-end PVC wall covering products, but are much more expensive than low-end vinyl. Table 7.4.3 M below summarizes the cost, choice, maintenance and environmental health and safety aspects of these alternatives.

Table 7.4.3 M: Materials Alternatives Assessment Summary for Wall Covering

Assessment Criteria		**DEHP/PVC Reference**	Comparison of Materials to DEHP/PVC					
			Glass Textile	Wood Fiber/ Polyester	Cellulose/ Polyester	Wood Pulp/ Recycled Paper	BioFibers	Polyolefin
Performance	Color/Pattern Choices	**Unlimited**	-	=	=	-	-	-
	Ease of Maintenance	**Easy**	=	=	=	=	=	=
Cost	Cost per yard (material only)	**$3 – $22/yd** (depends on quality)	=	=	=	=	?	=
Environmental Criteria	Derived from Sustainable Material	**No**	+	+	+	+	+	=
	Recyclable	**No**	=	=	+	?	+	+
	Compostable	**No**	=	?	?	+	?	=
	Teflon® Coated	**Possible**	+	+	=	+	-	-
Human Health	Exposure to Emissions During: • Manufacture • Installation • Use	**VOC emissions (M, I, U)**	= (U)	?	?	?	?	=

Comparison Key + Better = Similar - Worse ? Unknown

7.5. Summary and Conclusions

Di (2-ethylhexyl) phthalate (DEHP) is globally the most commonly used PVC plasticizer, used to impart flexibility into this otherwise rigid polymer. As a plasticizer for PVC, DEHP offers excellent compatibility and performance properties at a low cost. DEHP is found in a wide variety of flexible plastic products, and can be found in amounts ranging from less than 20% to more than 50% by weight.

DEHP is not chemically bound into the polymer matrix and therefore can migrate out of the polymer. It is lipophilic, so that in the presence of fatty solutions it will be more likely to migrate out of the polymer. DEHP has been shown to be a reproductive toxin to male rodents, and the CERHR has expressed "serious concern" about the potential exposure to human neonates. In addition, while it has a relatively low vapor pressure, the potential for worker and public exposure to DEHP that does volatilize into the air is a concern to public health advocates. Finally, it has been shown to be present in indoor air dust particles, especially in homes where PVC surfaces are prevalent. Although the scientific evidence of a direct link between adverse health effects and exposure to DEHP in air, dust or in solutions to which humans are exposed (*e.g.,* solutions injected into the body during medical procedures) has not been shown to be incontrovertible, both the public and the federal agencies charged with protecting public health express concern that health effects do exist.

The Institute looked at plasticizer and material alternatives to DEHP and DEHP/PVC blends used in resilient flooring, medical devices for neonatal care, and wall coverings. These uses were chosen because of their prevalence of manufacture and use in Massachusetts, as well as their potential to expose workers and the public to DEHP and its metabolites.

Resilient Flooring

Resilient flooring is used in residential, commercial and industrial settings. Many of these applications use DEHP/PVC blends. In fact, the largest user of DEHP in the Commonwealth manufactures resilient flooring for industrial applications.

The Institute identified and assessed four plasticizer alternatives and three material alternatives to DEHP/PVC. Each of the plasticizer alternatives assessed (DEHA, DINP, DGD and DEHT) exhibit equal or better EH&S profiles compared to DEHP. They also exhibit comparable costs and performance characteristics, though industry feels that cost is a limiting factor in the lower end industrial and commercial resilient flooring markets. In addition, it is likely that some processing modifications would be required in order to switch to an alternative plasticizer. This could present an initial capital cost to industry.

Of the three materials assessed as alternatives to DEHP/PVC, cork and linoleum appear to have equal or better EH&S, performance and cost profiles. Emerging recycling and infrastructure opportunities will improve this assessment for linoleum.

Medical Devices for Neonatal Care

DEHP is used in many different medical devices. The primary groups of medical devices are sheet (*e.g.,* IV and blood storage bags) and tubing devices. Based on the serious concern expressed by the CERHR for neonate exposure to DEHP via medical procedures, as well as the continuing debate over the actual exposure to DEHP and the associated health impact from these devices, the Institute limited its assessment to sheet and tubing devices used for neonatal care. The medical procedure that appears to present the highest potential for exposure to DEHP is extracorporeal membrane oxygenation, a procedure that is used only in neonatal care situations.

Sheet devices are used to store the following solutions: blood products (red blood cells, platelets and fresh frozen plasma), nutritional solutions (total parenteral nutrition and enteral solutions), intravenous solutions and drugs. The choice of plasticizer or material for a specific sheet device is highly dependant on the medical solution stored. Therefore no single alternative can be promoted for all potential uses. For red blood cell storage DEHP/PVC continues to be the material of choice, though BTHC/PVC has been FDA-approved for use in red blood cell storage. However BTHC is less amendable to steam sterilization than is DEHP and is significantly more expensive than DEHP. There is a continuing need for research to identify other plasticizer and material alternatives for this use.

TOTM, DEHA, BTHC and DINCH all appear to be potentially appropriate alternatives to DEHP for other medical solution storage options, though DINCH has not yet received FDA approval for use in medical products in the US. More research is required to determine the migration potential of these plasticizers into various solutions, and to assess the potential toxicology associated with exposure to these plasticizers and their metabolites in neonates. Modifications in processing requirements are likely to be associated with a switch to any of these alternative plasticizers. In addition, the cost of TOTM, BTHC and DINCH are relatively higher than DEHP

For tubing devices, DINP and DEHA were assessed as alternative plasticizers. Both are comparable in cost, with some processing and EHS issues that require further study before determining a preferred alternative to DEHP.

Several alternative materials were assessed for both sheet (EVA, polyolefins and glass) and tubing (polyolefins, silicone and TPU) applications. Products utilizing the alternative materials, either singly or in multi-layer laminates, are currently commercially available for sheet and tubing device applications with the notable exception of red blood cell storage. Many manufacturers are currently offering non-DEHP and/or non-PVC alternatives for both sheet and tubing uses.

Wall Coverings

Despite the relatively low vapor pressure of DEHP, public health advocates express concern that DEHP will volatilize into the air and/or be present in dust associated with DEHP/PVC (vinyl) wall coverings. The Institute assessed two plasticizer alternatives to DEHP: DEHA and DINP. Both DEHA and DINP appear to be technically feasible alternatives to DEHP in wall covering applications, exhibiting comparable EH&S, performance and cost profiles.

Numerous alternative materials were assessed, including woven glass textiles, a wood fiber/polyester blend, cellulose polyester blends, a wood pulp/recycled paper blend, biofiber products, and polyolefin/synthetic textiles. Each appears to present a feasible alternative to DEHP/PVC for wall covering applications.

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Chapter 8. Statewide Economic Impact

Five Chemicals Alternatives Assessment Study

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8.1 Overview

Part of the Institute’s mandate was to assess potential effects on the employment level and the economic competitiveness of the Commonwealth associated with adopting alternative chemicals or technologies. Cost considerations specific to individual chemicals and alternatives are discussed in the earlier chapters of this report, but this information is not evenly available and the cost for a material or chemical may depend on variable energy costs or material availability. Assessing economic effects also requires information on materials, labor, production, market and other data that may change over time. In addition, the employment and competitiveness implications of adopting an alternative are tied to the policy environment in which the alternatives adoption occurs. Voluntary adoption of alternatives, technical assistance programs, mandatory chemical phase-outs, or grant or loan programs designed to ease the transition to safer alternatives may all produce different market outcomes.

In order to make the best possible use of limited time and resources, the Institute did not attempt to draw firm conclusions about the employment and competitiveness implications of adopting the alternatives that are explored in this report. Instead, the Institute sought to identify major factors that influence the economic outcomes of adopting safer alternatives. The Institute briefly reviewed the experiences of the TURA program and the literature on the economics of environmental regulation and alternatives assessment, and held a day-long discussion session with selected economists and other experts in innovation and technology diffusion. A brief look at the five chemical assessments yielded additional insights. In this section the Institute offers a framework as guidance for users of this report on critical factors to consider when assessing the economic impacts of alternatives adoption. Appendix E contains more detailed discussion topics from the day-long session, as well as case materials, which serve to ground this topic with specific examples.

Introduction

The charge for this section of the alternatives assessment study was to:

> "Conduct an analysis of potential impacts on employment level and economic competitiveness of the Commonwealth from adopting and implementing any alternative chemical or technology as substitutes."

TURA Experience

The economic impacts of toxics use reduction in Massachusetts are explored in the 1997 program evaluation report of the Toxics Use Reduction Act (TURA) (Toxics Use Reduction Institute (TURI) 1997). This benefit-cost analysis found that economic benefits outweighed costs, even without accounting for increased revenue from capital investments in improved processes, benefits to non-TURA firms in Massachusetts from TURA program resources, or human health and ecological benefits. For the period from 1990 through 1997, the direct monetized benefits were found to be $90.5 million in 1995 dollars. The costs were found to be $76.6 million ($49.4 million in compliance costs, and $27.1 million for capital investments), so the net benefit was $13.9 million. Specific examples of cost savings are discussed in case studies that have been developed by the Institute and the Office of Technical Assistance for a number of companies, detailing the types of production changes that were undertaken and the yearly savings that were achieved as a result.[42] Some of these companies achieved toxics use reduction by improving efficiency of chemical use, while others adopted alternative chemicals or processes.

The TURA program requires large quantity toxics users to make a toxics use reduction plan that documents a mass balance of materials, considers safer options, and includes total cost accounting methods. Implementation of these plans is voluntary. The program evaluation found that TURA regulated firms have discovered opportunities that were both financially and environmentally beneficial and that might not have been discovered without the requirement to look for such opportunities. In addition, industry made use of and valued the training, informational support and technical assistance provided by government entities under the TURA program. Finally, TURA regulated firms have become leaders in efficient production, corporate environmental reporting, and management systems methods that make them more competitive.

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[42] Case studies are available on the website of the Massachusetts Office of Technical Assistance for Toxics Use Reduction, at http://www.mass.gov/envir/ota/publications/case_studies1.htm.

Literature Review

There is a substantial literature on the economic implications of pollution prevention, including many case studies of specific firms' experiences in adopting safer substitutes. This literature has been summarized elsewhere and is not reviewed here. As a context for the experts' discussion of the economic implications of alternatives adoption, the Institute briefly reviewed the literature on economic implications of environmental regulation.

Economist Michael Porter developed the hypothesis that strict government environmental regulation can promote efficiency and catalyze innovation, thus improving industrial competitiveness. This idea has been extensively debated since its publication in the 1990s (Ashford, 1999, Porter, van der Linde, Claas 1995). Many questions remain about the relationship between environmental regulations and economic competitiveness, as well as between the environment and economy more generally. This section summarizes some of the key parameters of the issue as developed by others.

The literature generally shows that costs for environmental performance improvement are overestimated, although there is some disagreement (Harrington, Morgenstern & et al. 2000, Hodges 1997, McGarity, Ruttenberg 2002, Office of Technology Assessment (OTA) 1995). Reasons for overestimation include lack of information, reliance on estimates from the affected industries, and a static approach to analysis that ignores learning effects and economies of scale (Ackerman 2006), as well as the potential for innovation. The process of estimating costs of any change in a facility is difficult and there are many unknowns. Also, there is no guarantee that innovation efforts will be successful (Lazonick). Many argue that the design of a particular regulation is an important determinant of its economic impact and/or effectiveness, and argue for technical flexibility regardless of whether strict or loose regulations are advocated (Ashford 2002, Majumdar 2000, Porter, van der Linde, Claas 1995).

Many studies have found that the overall state or national economic effect of environmental regulations is neutral (Ackerman 2006, Goodstein 1999, Meyer 1995). Among the reasons cited are (1) "regulation does not remove money from the economy, so much as cause it to be spent in different sectors,"(2) environmental regulatory costs are comparatively small in the context of other business cost factors, and (3) macroeconomic drivers such as Federal Reserve policy have an overriding impact. In addition, little evidence has been found to support the "pollution haven" hypothesis that firms move to areas of lesser environmental regulations (Ackerman 2006, Goodstein 1999). Factors such as wage rates, market access, and availability of skills and natural resources appear to dominate location decisions. However, even if neutral overall, there may very well be transitional difficulties caused by regulatory action, and impacts on individual firms may differ substantially from overall economic impact.

With environmental efforts, as in all other aspects of the economy, there will be gains and losses. Some companies will face reduced costs through environmentally beneficial process changes such as waste prevention and increased efficiency of chemical use, (Lenox, King 2002) and may gain competitive advantage through innovative and proactive responses to regulation or environmental issues (Clarkson, Li & Richardson 2004, Porter, van de Linde, Claas 1995). Other companies may be hampered by regulatory costs and become less competitive under changing regulatory and market environments (Clarkson, Li & Richardson 2004, Joshi, Krishnan & Lave 2001). Some regulations may have a disproportionate effect on small businesses (Crain, Hopkins 2000, Dean 2000). Radical innovation may benefit the economy as a whole, but put existing dominant industries at a competitive disadvantage (Ashford 1999).

Another important area of literature deals with the economic costs associated with preventable illnesses that result from toxic exposures. Although these are very difficult to quantify, studies at the national and the state level have estimated the costs of environmentally attributable illnesses. In addition to the direct costs of treating preventable illnesses, these figures include the costs to employers of workers' compensation and work days missed, the costs to families of institutional or home care for individuals who are ill or disabled, the costs to state and local budgets of special education services, and the costs of productivity losses over the lifetime of affected individuals (Davies 2005, Fahs, Markowitz 1989, Landrigan, Schechter 2000, Massey, Ackerman 2003, Salkever , Trasande, Landrigan 2005, Waitzman et al. 1995, Waitzman, Romano & et al. 1994).

Expert Discussion Group

The Institute convened a group of experts to discuss the economic factors involved in determining the possible economic impacts of adoption of safer alternatives and the variety and scope of possible impacts. Participants were chosen for their economic and development expertise relating to industry, labor, innovation, and environmental economics, and included:

- Stephen J. Adams, Small Business Administration
- James Goldstein, Tellus Institute
- William Lazonick, University of Massachusetts Lowell
- Teresa Lynch, Economic Development Research Group
- Edward March, University of Massachusetts Lowell
- Andre Mayer, Associated Industries of Massachusetts
- Deborah Savage, Environmental Management Accounting Research & Information Center

Three others were not able to attend the meeting but were asked for their perspectives, and their comments were incorporated into this report. These were:

- Frank Ackerman, Global Development and Environment Institute, Tufts University
- Michael Goodman, Donahue Institute, University of Massachusetts Boston
- Christopher Tilly, University of Massachusetts Lowell

Case material (Appendix F) helped to ground the discussion with examples for the following sectors: formaldehyde in building materials, lead in electronics, and perchloroethylene in dry cleaning. These sectors were selected as useful, representative, and well-documented examples that represent three different scenarios for Massachusetts; *i.e.,* a product that is manufactured elsewhere and imported into the state (building materials), a product that is manufactured in the state and exported elsewhere (electronics), and a local business conducted entirely within the state (dry cleaning). These were characterized as import, export, or local industries to describe the supply chain perspective and other market dynamics.

Table 8.1 describes the three cases in terms of the significant factors identified by the panel.

Table 8.1. Panel observations on case study characteristics

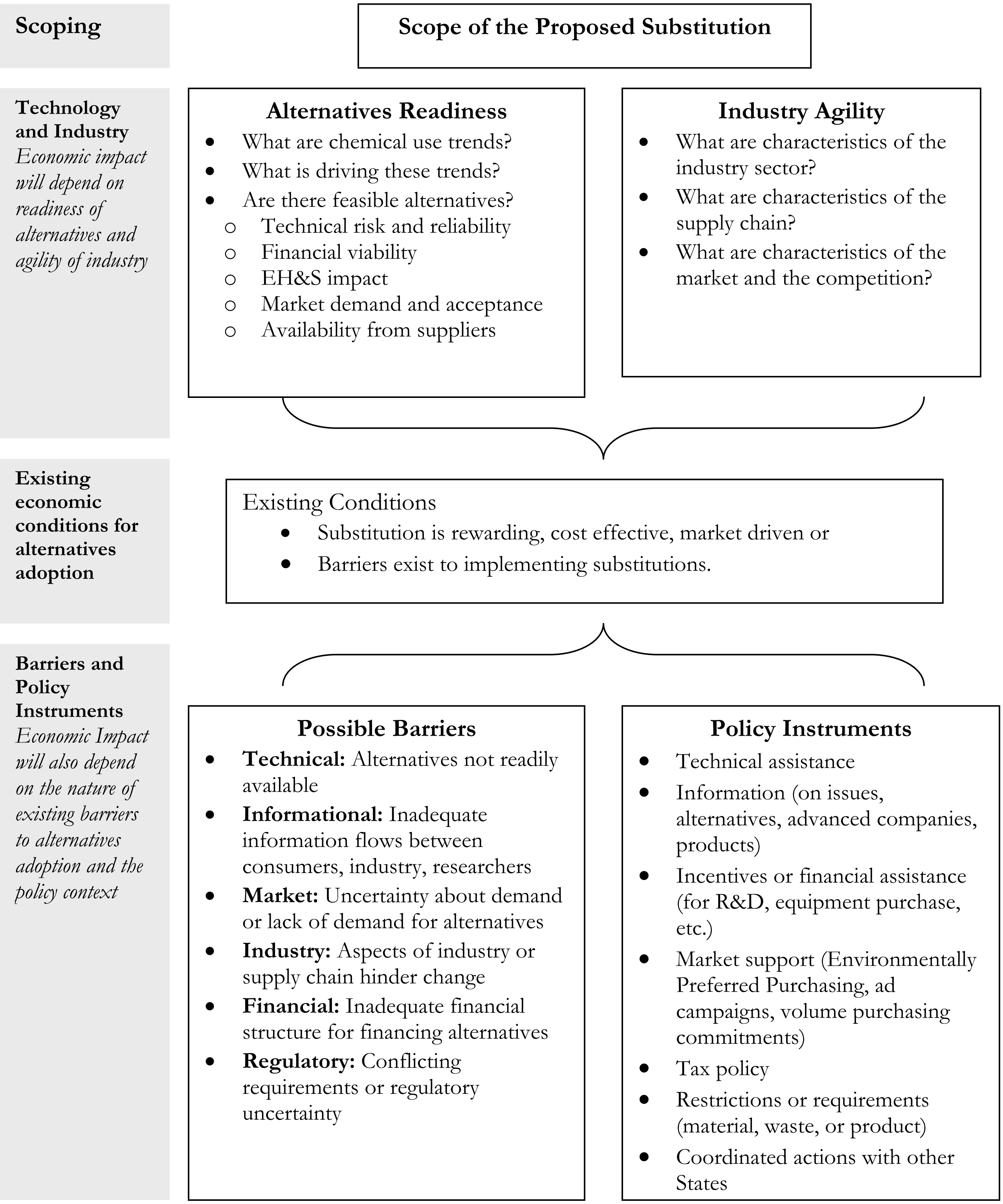
Industry	PCE in Dry Cleaning (local)	Lead in Electronics (export)	Formaldehyde in Building Materials (import)
Supply chain	• Local service • Machine and chemicals imported into MA. • 5-6 PCE manufacturers (all outside MA).	• Imports: finished products and components • Exports: high-end. • Complex international supply chain.	• Primarily import products • Limited export and local • manufacture
Availability and cost of alternatives	• Many alternatives • Alternatives more and less costly than existing	• Alternatives agreed on • Long-term performance and environmental issues not well understood	• Some products have readily available alternatives, others do not. • Alternatives not widely used or available
Chemical use trends	• National decline of use • Adoption of PCE-free alternatives slow	• Decreased use of lead in electronics applications	• Green building movement expanding rapidly • Low off-gas formulations increasing
Existing drivers	• California regulations and incentives • Consumer demand •	• Regulations in European Union (RoHS), California, and China • Customer requirements	• Concerned consumers • Green Building, increasing interest in LEED Certification.
Industry	• >90% Small family businesses, immigrant • Few suppliers of machines and chemicals	• Many companies of all sizes • Many specialty niches	• Numerous contractors and manufacturers of all sizes • Many products regionally distributed
Financial	• High-cost long-life machines • Financing often assisted by trade associations	• Higher energy costs • Capital cost for new processing equipment and product redesign	• Consumer construction loan financing (banks) • Durability and resale value important.
Market and competition	• Majority of consumers price sensitive • 10% high-end customers • Not a Massachusetts competitiveness issue.	• Significant international competition on the basis of price or technology • Massachusetts cannot compete on price, must compete on technology	• Market segments: residential, commercial, institutional • Residential more difficult to affect • Competition highly product or application dependent

8.2. Economic Impact Assessment Framework

The economic experts' discussion yielded a broad framework for conducting an economic analysis of alternatives adoption. Future projects could be designed to provide much of the specific information needed for an analysis of this kind. This framework is presented in Figure 8.2.

Figure 8.2. Economic Impact Assessment Framework

This framework outlines the ways in which alternatives adoption may affect jobs, industry, and other aspects of the economy.



Scoping

Scope of the Proposed Substitution

Technology and Industry
Economic impact will depend on readiness of alternatives and agility of industry

Alternatives Readiness

- What are chemical use trends?
- What is driving these trends?
- Are there feasible alternatives?
    - Technical risk and reliability
    - Financial viability
    - EH&S impact
    - Market demand and acceptance
    - Availability from suppliers

Industry Agility

- What are characteristics of the industry sector?
- What are characteristics of the supply chain?
- What are characteristics of the market and the competition?

Existing economic conditions for alternatives adoption

Existing Conditions

- Substitution is rewarding, cost effective, market driven or
- Barriers exist to implementing substitutions.

Barriers and Policy Instruments
Economic Impact will also depend on the nature of existing barriers to alternatives adoption and the policy context

Possible Barriers

- **Technical:** Alternatives not readily available
- **Informational:** Inadequate information flows between consumers, industry, researchers
- **Market:** Uncertainty about demand or lack of demand for alternatives
- **Industry:** Aspects of industry or supply chain hinder change
- **Financial:** Inadequate financial structure for financing alternatives
- **Regulatory:** Conflicting requirements or regulatory uncertainty

Policy Instruments

- Technical assistance
- Information (on issues, alternatives, advanced companies, products)
- Incentives or financial assistance (for R&D, equipment purchase, etc.)
- Market support (Environmentally Preferred Purchasing, ad campaigns, volume purchasing commitments)
- Tax policy
- Restrictions or requirements (material, waste, or product)
- Coordinated actions with other States

The following sections provide more detail about the major headings found in Figure 8.3.

Scope of the Proposed Substitution

Alternatives Readiness

What are chemical use trends?

Chemical use trends can be described and listed as uses, geographic locations, and impacts and quantified as volumes and substitution rates.

What is driving these trends?

There may be a number of existing drivers for substitution, including better quality or less expensive alternatives and changes in regulation or consumer preference. Detailed information may include

- Costs – *e.g.*, the cost of disposal of toxic waste, chemical prices or use taxes
- Market changes -- *e.g.*, export market requirements, local consumer demand, company brand image protection, or customer programs in Environmentally Preferable Purchasing
- Innovation – *e.g.,* the obsolescence of existing equipment
- Regulation – *e.g.,* the European Union WEEE and RoHS Directives
- Financing/Insurance – *e.g.,* service providers requiring risk reduction

Are there feasible alternatives?

Technical, financial, and EH&S considerations for each alternative must be researched, including market and supply.

Industry Agility

What are characteristics of the industry sector?

Characteristics to consider include size (number of employees or annual sales), ownership, the education and skill levels of workers as well as their salary ranges, some measure of innovativeness, profit margins and investment practices.

Availability of capital is part of a broader picture of facility investment in an alternative, including the timing of such a transition, the value and remaining lifetime of any existing investments, and the hurdle rate used to make investment decisions.

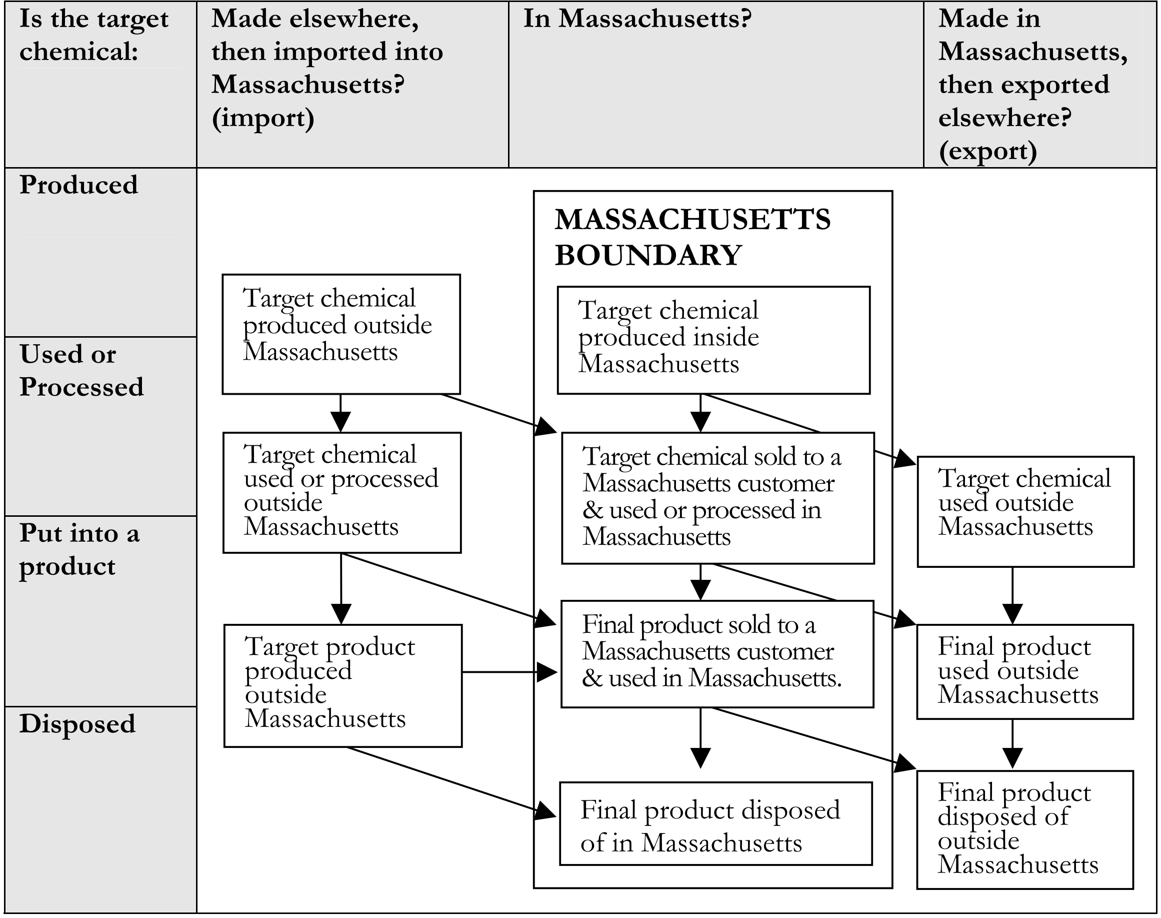
What are characteristics of the supply chain?

Are products containing substances of concern imported or exported, or are the products primarily local to Massachusetts? Who are suppliers and customers, and where and how large are they? Are trading partners large enough to influence the industry sector?

The location of Massachusetts in the supply chain will affect the degree and nature of Massachusetts influence on the market in a given chemical or alternative. It is also important to identify the actors that have most influence on the industry. These may include suppliers that provide information, banks that provide financing, or customers who demand a product change.

The charts below illustrate supply chain characteristics for two of the case studies as developed by one of the expert reviewers. The first chart, Figure 8.3A**,** provides a general schematic to help in visualizing supply chain dynamics, and the subsequent figures provide examples.

Figure 8.3 A -- Supply Chain General Schematic



In the case of PCE use for dry cleaning services, Figure 8.3B, Massachusetts is an importer of dry cleaning machines, but dry cleaning is a local process. As an importer, Massachusetts may not have sufficient market size to drive development of non-PCE machines on its own. However, given that California regulation and technical assistance programs are already driving commercialization of alternatives, Massachusetts action could speed the process of adopting these alternatives.

In the electronics sector, Figure 8.3C, Massachusetts manufactures components, assembles high-tech equipment, and consumes components and equipment. In the first two cases Massachusetts is an exporter, and must respond to international market drivers in order to remain competitive. Component manufacturers must be aware of demand for lead-free components, as well as supply costs, the extent of EU demand, and location decisions.

Figure 8.3. B -- Massachusetts Perchloroethylene Drycleaners – "Local" Supply Chain Example

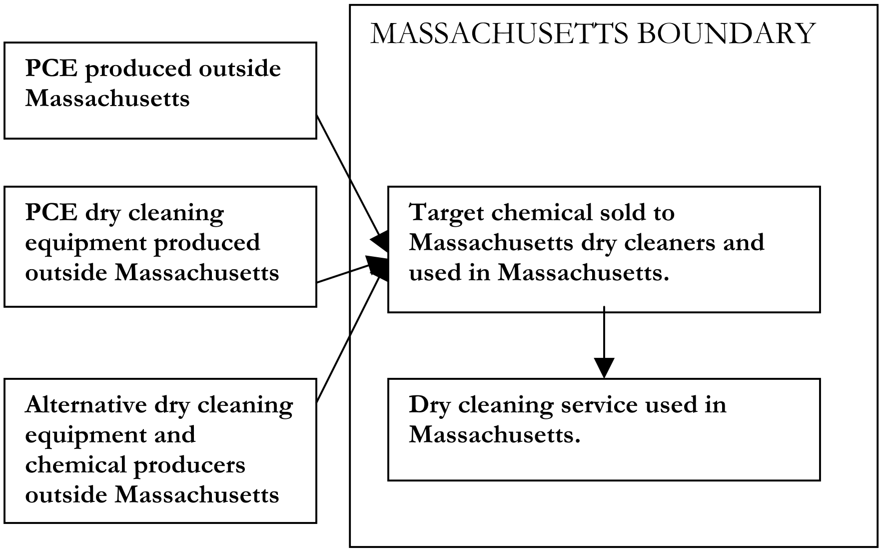
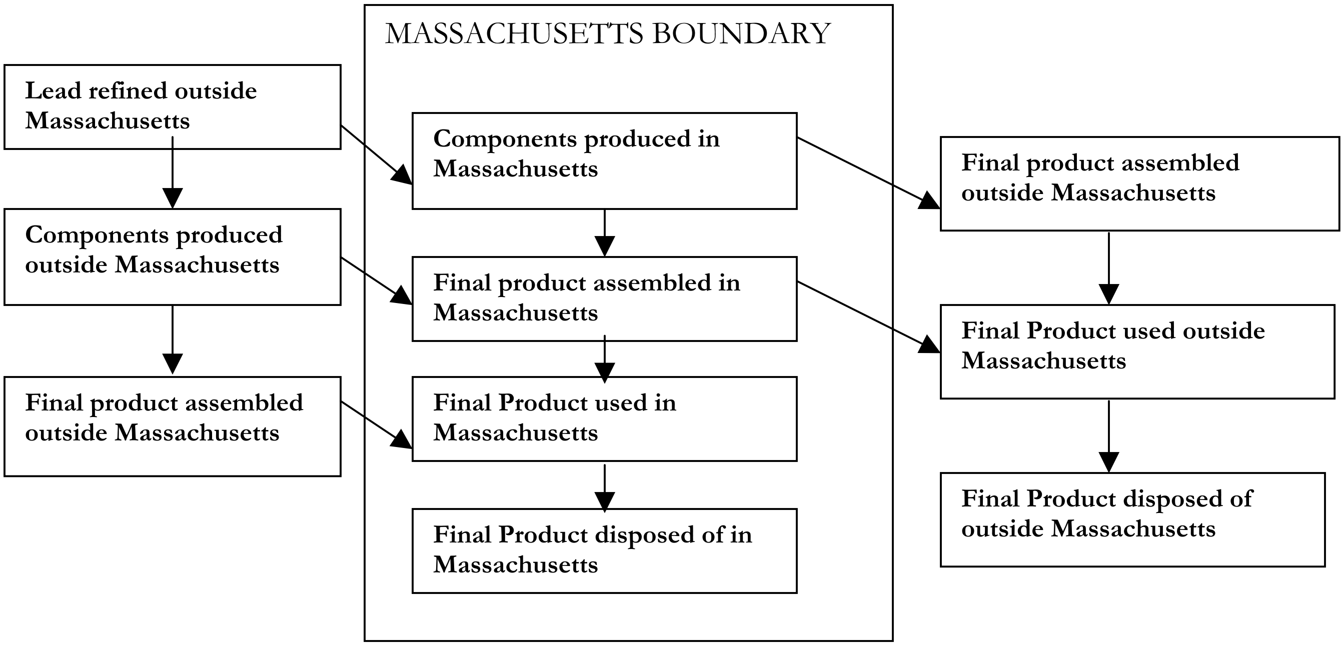


Figure 8.3 C -- Massachusetts Lead-Free Electronics – "Export" Supply Chain Example



What are characteristics of the market and the competition?

A shift to alternatives may raise or lower costs of producing a product or providing a service. Market characteristics will determine the extent and form of resulting economic impacts. Factors to consider in assessing the influence of competition and markets include the following:

- Is the market local, regional, national or international?

- What is the size of the Massachusetts market vs. other locations?
- Does Massachusetts compete based on location, price, and product quality?
- How much does a change in price affect demand?
- How important are non-price characteristics, such as brand image and quality?
- Are there market niches that would respond differently to changes?
- What existing regulations influence the industry?
- How frequently does the market require a new or improved product?

In some cases there may be product niches that can be capitalized for developing greener alternatives, while in other cases the market structure may prevent charging a premium for green innovations. Market divisions may respond differently to changes. For the building materials case (formaldehyde), experts suggest that residential, commercial, restorative, and institutional building markets have different characteristics. Green building practices are being adopted more quickly in institutional and commercial buildings. These customers have better access to information about alternatives than residential customers. Markets with rapid product turnover are more likely to be able to respond quickly to changing requirements.

Factors important to a firm's ability to adapt to changes are summarized in Table 8.3.

Table 8.3: Industry Status and Trends Summary Table

Industry	Supply chain	Competition & Market
• Size • Ownership • Workforce • Profit margin • Innovation • Investment Practices	• Import/export/local • Suppliers & customers • Partner influence	• Competitive basis • Price elasticity • Market influence • Market divisions • Regulatory environment • Speed of market change

Existing Conditions

Understanding the availability of alternatives and the agility of industry gives an indication of the existing economic conditions for alternatives adoption. In some situations substitution may already be rewarding, cost effective, market driven, and proceeding on its own. In other situations, barriers exist to implementing substitutions, and use of old alternatives continues.

Possible Barriers

The third phase of this economic assessment involves consideration of existing barriers, as well as the policies which can address these barriers and facilitate adoption of alternatives.

Technical Barriers: Alternatives not readily available

As this study demonstrates, for some chemicals and some uses alternatives are well understood and readily available. In other cases, fully-developed alternatives may be unavailable at the outset. In other instances, alternatives may be well developed from the perspective of researchers and a few leading companies, but there remain technical, reliability, cost, and risk concerns for most companies.

In cases in which alternatives are not well developed it is helpful to understand (a) the relevant time-frame for transforming costs into benefits, (b) whose interests will be served by a focus on innovation in this area, and (c) if public funds are used for research, the institutional mechanisms for ensuring that public investment results in public benefits when the innovation is successful.[43]

Information Barriers: Inadequate information flows among consumers, industry, and researchers

Lack of information can be a barrier to change. The TURA Program has demonstrated the effectiveness of providing training and information on alternatives to businesses. Information can also be provided to consumers through labeling, product guides, advertising, and certification for contractors and products.

Market Barriers:

Uncertainty about demand or a lack of demand for alternatives can hinder a firm from moving forward into new technologies. Other industry characteristics that can hinder alternatives adoption include low profit margins or a volatile price environment, lack of necessary expertise among workers, or an industry culture resistant to change.

Financial Barriers: Inadequate financing structure

In cases in which alternatives adoption requires a significant capital investment, lack of adequate financing can be a barrier. Studies suggest that environment-related investment costs and savings are not often considered adequately in firms' investment analyses. Some approaches to book-keeping may hide the costs of using toxic chemicals, or may consider these costs in a separate department. Mayers (2005) suggests that more time be "spent re-engineering business accounting systems to accurately track environment-related costs (and returns) and determine where substantial cost-savings can truly be found." Other potential financial barriers may include lack of familiarity with alternative technologies among finance providers.

Regulatory Barriers: Conflicting requirements, regulatory uncertainty, unregulated competitors

Sometimes adoption of alternatives is delayed because it is unclear whether a regulation will hold. Some companies will delay action if they view pending future regulation as changing the playing field in an unpredictable way. Conflicting regulatory requirements may hinder industry action. For example, the use of drawer sanitizers in salons is required by regulation in Massachusetts.

Policy Instruments

The interactions among policies may be mutually reinforcing, redundant, or conflicting. Policies that influence economic impact can include:

- Technical assistance and training
- Information provided on technology and methods issues, alternatives, leading companies, products, tools, and legislation for Massachusetts companies and for consumers. Particularly helpful is advance information about trends and pending science and policy.[44]

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[43] The Sixth EU Framework Programme for Research and Technological Development (FP6) has explicit language requiring proposals include a "plan for use and dissemination' to show that knowledge generated will be successfully exploited and there is an 'obligation to use and disseminate the results of the project' within a set time. (European Union, 2006).

[44] The state offers an array of informational tools as part of the Commonwealth of Massachusetts Environmentally Preferable Products Procurement Program.

- Incentives or financial assistance for research and development, equipment purchase, *etc.*
- Market support through Environmentally Preferred Purchasing programs in government, advertising campaigns, and volume purchasing commitments
- Tax policies
- Restrictions or requirements for use of targeted materials or products
- Coordinated actions with other states

There is a substantial body of literature about environmental policy options, including writings about market-based vs. traditional regulatory approaches. The policy options included here are ones that were discussed by the panel and described in the text where appropriate; it is not a comprehensive listing.

8.3 Economic Themes

The TURA experience, research and the panel discussion yielded important themes that are relevant to the Legislature's charge.

- **Protecting human health:** Economic benefits of public health improvement resulting from safer alternatives may be overlooked because they are difficult to quantify, but they are very significant. The impact of a reduction in these costs was not extensively discussed by the panel, though many stated that they wanted to see this addressed.

- **Identifying economic opportunities:** There may be economic opportunities in environmental improvement.

- **The Commonwealth as convener:** The Commonwealth can play a useful role in facilitating industry problem-solving. There is substantial evidence supporting strategies that bring industry and universities and trade associations together, and help industry problem-solvers make the case for change.

- **Economic outcomes are uneven:** Not all companies benefit from business opportunities created by new technology, regulations, incentives, or other conditions. Regardless of whether the overall state-level impact of a change is found to be positive, negative, or neutral, there will be economic winners and losers. For example, a trend toward capital-intensive CO_2 dry cleaning would favor larger dry cleaners, whereas a trend toward labor-intensive wet-cleaning would favor small businesses, regardless of whether the shift from perchloroethylene dry cleaning was regulatory or market driven.

- **Supporting small businesses:** Small businesses were recognized as important to innovation, employment and entry into business ownership . They also may be disproportionately affected by environmental regulation (as well as other factors for which economies of scale are important). At the same time, if small businesses are not ready for upcoming transitions (such as international regulations like the European Union Restriction on certain Hazardous Substances Directive, "RoHS") they may lose business. If businesses in the state are ahead of these transitions and able to meet requirements or new market demands more quickly or cheaply, companies may gain business.

- **Maintaining a range of job types:** Research and development spending, manufacturing facilities, and regulation may or may not create and maintain good jobs in the state. Research support may not directly address employment for less educated workers, although through a multiplier effect it can lead to greater demand for less skill-demanding jobs such as waitstaff or other support to professional and technical workers.

Manufacturing facilities that currently provide middle-class wages for lower-education jobs in Massachusetts today are vulnerable, and workers may benefit from advanced training to earn middle-class wages in manufacturing in Massachusetts. Business consolidation (e.g. larger dry cleaners) may cause the loss of small immigrant-owned entrepreneurial businesses.

- **Flexible options:** Technical assistance programs are helpful in supporting positive economic outcomes from substitution, as are preferred purchasing programs, information dissemination, capital financing assistance, government assisted research, and labeling programs like Energy Star. However, voluntary options may leave behind more marginal companies and concentrate negative impacts on the economically disadvantaged.
- **Influence of Regulatory Policy:** Regulatory action may influence the economic impact of alternatives adoption under different circumstances. Many areas of disagreement remained among panel members concerning the significance of these circumstances, which can be organized as follows from the perspective of supply chain and availability of alternatives.

Imports

In cases where Massachusetts is an importer of goods, the issue is the extent to which companies will need to cater to unique demands from the relatively small Massachusetts market in the following situations:

- If alternatives exist but are not available, the Massachusetts market alone **is likely** to be large enough to provide a market incentive for companies to improve distribution of these alternatives
- If no alternatives exist and Massachusetts is an importer of goods, the Massachusetts market alone **is unlikely** to be large enough to provide a strong market incentive for companies to develop new alternatives. There was discussion about whether California was large enough, and agreement that the European Union definitely was, as evidenced by the Restrictions on certain Hazardous Substances Directive "RoHS" and the Waste Electrical and Electronic Equipment Directive "WEEE". It was agreed that states working together, *e.g.,* New England and New York, could make a bigger market that could influence alternatives. The possibility was discussed of creating a market niche that ultimately substitutes a locally developed product for what was previously an import product, thus creating a new export industry.

Exports

In cases where Massachusetts is an exporter of goods, the issue is the competitive position of Massachusetts manufacturers in national or global markets. There is significant disagreement over whether unique Massachusetts requirements for manufacturing processes and products put Massachusetts companies at a competitive advantage or disadvantage. The different viewpoints include:

Disadvantage

- Massachusetts-specific requirements where there are existing global requirements could add expense rather than help companies meet challenges.

- Added costs for reducing or eliminating certain toxics that the global market does not require could reduce competitiveness.
- Whether Massachusetts policy appears to industry to be relatively restrictive or inviting might influence company location, expansion, or investment decisions.

Advantage

- Massachusetts requirements could help Massachusetts companies meet global challenges such as RoHS and forthcoming requirements elsewhere.
- Costs of regulations are often less than anticipated, and thus do not, in actuality, reduce competitiveness.
- There is no or little evidence to support the claim that regulatory climate is a key determinant of companies' decision-making around locating and/or investing in facilities.

Local

In service-industry cases, for example dry cleaning, auto-body, or hair salons, and certain other industries, such as cement, the market is local. Out of state purchases of the service or product are rare other than in border towns.

While there is agreement that larger markets have more influence than smaller ones, there are some disagreements on the implications of that fact for Massachusetts. Many of the reviewers agreed that an approach of collaboration with other states, such as in past efforts to reduce mercury, or ongoing efforts to reduce greenhouse gases, would help reduce costs. However there were disagreements over effects where Massachusetts sets policy ahead of other state and national initiatives, and there was some concern whether other states and countries would follow such initiatives. Whether or not other states would follow a leading state-level policy is an area of analysis for which there is extensive literature and debate but no consensus.

- **The role of innovation is an issue**. Massachusetts currently has an innovation advantage driven by major private research universities and high technology industries such as biotech, polymers, defense, and electronics. However, the degree to which the Commonwealth has a significant influential role in developing or maintaining industrial competitive advantage is less clear.

  There is evidence that Massachusetts companies could be helped to be innovative environmental leaders that use advanced technology to increase competitiveness while simultaneously meeting more stringent environmental standards. There is capacity here: the Commonwealth's existing knowledge base in both universities and companies offers unique high-tech capabilities with which to take advantage of emerging market opportunities for safer technologies. Public policy is needed to help build and maintain an advantage as, according to one expert, "…state subsidy is in virtually all places and at virtually all times integral to the innovation process." (Lazonick) However, it is possible that responding to market conditions rather than to government mandates is more economically attractive. State funded studies to identify emerging opportunities and ensure the high quality of the regional educational system in environmental technologies may have the best chance to increase competitiveness.

  Research on the innovative process is discussed further in Appendix E.

8.4 Lessons from the Five Chemical Assessments

Financial considerations and available information have been presented earlier in the course of each chemical-specific alternatives assessment. The information presented for each case varies according to context. For example, the price of materials is an important parameter for some cases, while operation, maintenance, or disposal costs may be salient for other cases. The Institute intentionally selected chemical uses for which some viable alternatives were expected to be available, and for which a detailed assessment of the technical, financial, and environmental health and safety characteristics of those alternatives was expected to be useful. In every case, the assessment showed that at least one alternative was commercially available, was likely to meet the technical requirements of many users, and was likely to be preferable from a human health and environmental perspective. Based on the Institute's experience with the uses discussed in this report, some broad patterns can be identified.

1. Some alternatives can be adopted without any adverse effect on Massachusetts employment or competitiveness. The formaldehyde alternatives assessment, for example, shows that elimination of formaldehyde dry sterilant from use in Massachusetts hair salons would produce savings and still achieve the desired level of sanitation. Similarly, Massachusetts schools could adopt alternatives to formaldehyde-fixed dissection specimens without increasing costs. The DEHP alternatives assessment notes that nearly all vinyl wall covering sold in the US today is manufactured in China and Southeast Asia. Many of the alternative wall covering materials are produced in the U.S.; thus, increasing demand for these alternatives could benefit domestic producers. Where Massachusetts firms have capacity for innovation, this is an opportunity.
2. Massachusetts manufacturers could gain market share through adoption of some alternatives. For example, some Massachusetts firms are working to produce DEHP-free medical devices. With growing demand for such devices, Massachusetts firms have the opportunity to develop this market niche. Another example is the potential competitive advantage of those wire and cable firms that have eliminated lead in their products, and now stand ready for markets in Europe and Japan that restrict this chemical.
3. Some alternatives require capital investment at the outset. For some technologies, this investment will pay for itself over time in reduced operating costs. For example, many of the alternatives to chromium plating offer technical production advantages that can yield significant savings for firms in the medium term. Many existing case studies of pollution prevention efforts by firms in Massachusetts and elsewhere document the savings that can be achieved through adoption of safer technologies. In contrast, some investments in safer alternatives may not be feasible for small businesses in the absence of targeted grant or loan programs. For example, a small dry cleaner that has recently purchased equipment for cleaning with PCE may not be able to convert to a safer alternative without assistance.

8.5 Conclusions

This chapter supplements the specific cost discussions in previous chapters with a broader consideration of economic patterns. It was not possible for the Institute to draw conclusions about the general employment or competitiveness impacts of alternatives adoption, but several broad lessons emerge.

First, there is strong evidence that adoption of safer alternatives can produce economic benefits, especially for those supported by the current market. This is a lesson from the experience of the TURA program, the literature on this topic, and some of the sectors considered in this report.

Second, there are some cases in which substituting chemicals or processes may have negative effects on some firms, even if there is a positive or neutral effect on the state economy more generally.

Third, there are many opportunities for government to support a positive economic outcome and to mitigate any negative effects for individual firms. In some instances, targeted assistance to industry can facilitate adoption of safer alternatives that will yield employment and competitiveness benefits over time. Government can have a role to play in facilitating adoption of alternatives that require an initial capital investment. Loan or grant programs may be particularly useful for small and medium sized enterprises. For example, California has demonstrated the viability of grant programs in facilitating the transition to safer alternatives for small dry cleaning facilities. Partnerships in research and skills development can also enhance knowledge of emerging safer technologies.

Finally, the framework presented in this chapter can be used to analyze likely economic impacts from alternatives adoption by clarifying the situational characteristics and factors that determine the outcome.

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Chapter 9. Conclusions and Recommendations

Five Chemicals Alternatives Assessment Study

Table of Contents

9.1 Conclusions

This report presents the results of alternatives assessments performed for several uses of each of five toxic chemicals. Through the preparation of this report, the Institute has learned both about the applicability of these specific alternatives *and* about the suitability of alternatives assessment as a methodology for informing toxic chemical use reduction.

9.1.1 Conclusions regarding the specific chemicals

The Institute performed alternatives assessments for 16 different use categories of the five chemicals. The Institute intentionally selected chemical uses for which some viable alternatives were expected to be available, and for which a detailed assessment of the technical, financial, and environmental health and safety characteristics of those alternatives was expected to be useful. In every case, at least one alternative was identified that was commercially available, was likely to meet the technical requirements of many users, and was likely to have reduced environmental and occupational health and safety impacts compared with the base chemical.

Many of the alternatives use chemicals that have been less thoroughly studied than the base chemicals, however, so their actual environmental and occupational health and safety impacts are less well understood. History presents many examples of chemicals that were thought to be relatively benign when first introduced but were later discovered to present significant problems (*e.g.* ozone-depleting chemicals, carbon tetrachloride as a degreaser).

The financial picture is mixed. Some alternatives clearly were cost-effective compared to the current process (*e.g.*, salon drawer sanitizer elimination). Some involve significant capital costs for implementation but are likely to have positive net present values due to operating cost savings (*e.g.*, high velocity oxy-fuel vapor deposition as a substitute for hard chromium electroplating). Some were clearly more expensive at this time (*e.g.*, vapor degreasing solvent alternatives), and for many, particularly the emerging technologies, no cost conclusions could be reached due to a lack of information. There are also cases where the alternative is more expensive but the cost differential is unlikely to have a significant impact on consumers, businesses or industry. For example, the cost of medical device tubing is a minor part of the cost of neonatal surgery.

9.1.2 Conclusions regarding the alternatives assessment process

Alternatives assessment is at the heart of the planning process established under the Massachusetts Toxics Use Reduction Act (TURA). The success of Massachusetts companies in reducing their use of toxic chemicals provides strong evidence that alternatives assessment works. We now have both a more robust methodology for that type of assessment, and results for selected uses of the five chemicals that will provide a useful starting point for further user-specific investigation. The information contained in this report indicates that alternatives assessment is a useful approach to evaluating toxic chemical use.

The active involvement of all stakeholders was key to the success of this project. Their expertise, willingness to collaborate and share perspectives, and review of the report were invaluable. The involvement of a wide range of stakeholders throughout the project resulted in a more accurate assessment, more valuable results, and increased understanding of the issues, challenges and perspectives among stakeholders.

In a broader sense, transparency was essential to the successful completion of this project, and is key to any successful alternatives assessment. This document can be used by others as a basis for their own work on alternatives, because the information we gathered is provided in the document. Judgment was used in assigning comparison symbols (+, - ,=, and ?) in the summary tables; therefore readers should use these summary tables to get a quick overview of important issues, and then consult the text and supporting tables for a full discussion. The Institute clearly stated situations where we were not able to gather full information on a given parameter.

Alternatives assessment rests on a three-legged stool – the technical, financial, and environmental and occupational health and safety (EH&S) performance of each alternative. One key to the success of this project was the use of a set of consistent, objective criteria in each performance category. This approach helped to ensure consistency of results from one assessment to the next.

Although the Institute is convinced of its utility, alternatives assessment is not without its difficulties. One significant difficulty is the selection of performance criteria for the EH&S evaluation. There are dozens of end points that could be considered (*e.g.*, carcinogenicity, mutagenicity, LD_{50}, flash point), and conflicting reasons to select many of them or just a few. Selection of a few criteria simplifies the analysis, but leaves the distinct possibility that a crucial category may be neglected. On the other hand, selecting a large set of criteria increases the analysis effort concomitantly, and introduces the new problem of aggregating and comparing the information across all of the categories.

In this study the Institute opted for a fairly large set of performance criteria, collecting data for the study chemical and its alternatives for 41 EH&S endpoints. Rather than attempting to combine these endpoints into one EH&S rating, this report presents the data for each alternative in tabular form, so that readers can make their own judgments about the environmental and occupational health and safety of the alternatives as compared to the study chemical.

Another difficulty with using alternatives assessment is the availability of full and objective information. Technical performance and cost data may be available for well-established technologies, but much less so for emerging ones. Similarly, the lack of EH&S information for newer chemicals reduces confidence in assessment results.

9.1.3 Conclusions regarding statewide economic impact

The panel of experts convened for this project were challenged with bringing their expertise to the complex topic of statewide economic impact from the adoption of alternatives. The framework created will assist users in analyzing likely economic impacts by clarifying the situational characteristics and factors that determine the outcome. Characteristics that may help to determine the economic implications of alternatives adoption include the size of the Massachusetts market in comparison with other markets, price sensitivity of consumers, nature of barriers to adoption, capacity of the workforce, and availability of useful and timely information.

9.2 Recommendations

The Institute's experience in completing this project leads us to the following recommendations:

- Numerous promising alternatives were identified during this study. Many of these will require further work to determine their practicality and applicability for specific applications. Such work will speed up the adoption of these alternatives, and could include detailed discussions with vendors and users, independent laboratory testing of technologies, pilot-scale industrial installations, supply chain workgroups and demonstration sites. The Institute has had success using these approaches for industrial toxics use reduction, and believes that there are many parallels for small businesses and consumer products. Examples of potential follow-up and additional research needs include:
  - Automotive aerosol cleaners (obtain further technical performance and EH&S data on alternatives)
  - Formaldehyde-free building materials (conduct basic research on new products and obtain associated EH&S data)
  - Formaldehyde salon sanitary storage (work with salons, regulatory agencies and vocational schools)
  - PVC in medical devices (conduct technical performance of the alternative plasticizers and alternative materials and obtain associated EH&S data)
  - Lead-free fishing sinkers (work with supply chain, including manufacturers, distributors, retailers, state agencies and sport fishing associations)
  - Alternatives to hexavalent chromium plating and passivation of zinc (conduct independent technical evaluations of the many emerging technologies)
- Both the TURA program experience and the Institute's experience in performing this project illuminate the positive gains that can be made if the Commonwealth, industry, and the public work together in a proactive fashion to identify and solve problems. The Institute recommends that any further efforts to address alternatives assessment incorporate and encourage this cooperative approach.
- Alternatives assessment shows great value as a methodology, but its utility would be improved by the use of a consistent set of assessment criteria from one assessor to another. The Institute has been working with its sister institute, the Lowell Center for Sustainable Production, in the development of such a standardized methodology. Various other groups in the United States and other countries use similar but somewhat different methodologies. The Institute recommends that the Commonwealth take a leadership role in this area and that an international working group be convened to establish and publish an agreed-upon standard alternatives assessment methodology.

Finally, this study will have been a success if it spurs discussion and debate. It is our hope that the objective information in this report will serve as valuable source material for those discussions. Everyone can agree that the goal of reducing the use of toxic chemicals is admirable – it is the best path to that goal that is frequently hidden or disagreed upon. For several specific uses of five toxic chemicals, this report should point the reader to promising paths. Uncovering the best path will require the active and creative cooperation of government, industry, and the public.