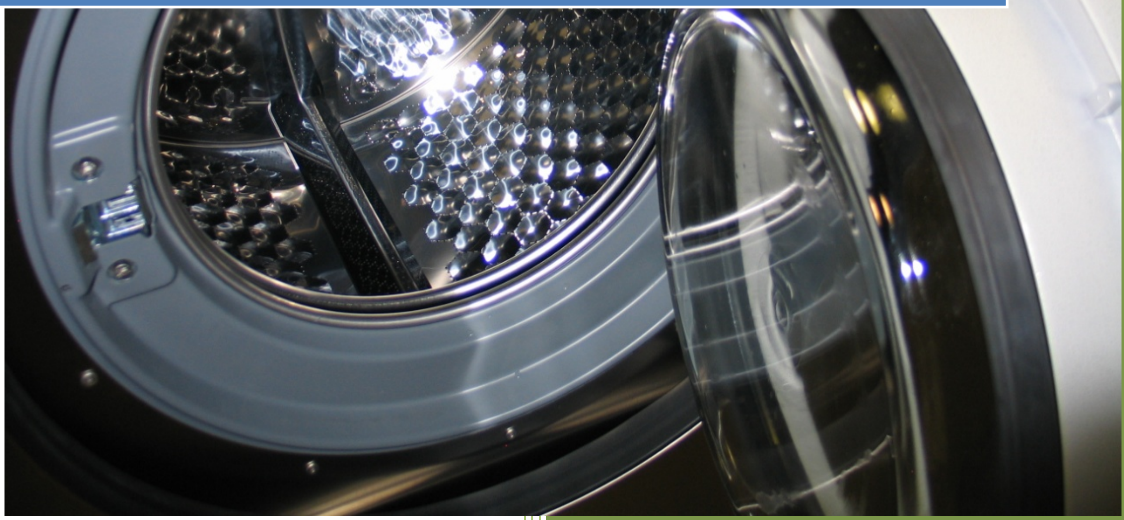
Assessment of Alternatives to Perchloroethylene for the Dry Cleaning Industry



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Contents

Acronyms and Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
ASME	American Society of Mechanical Engineers
ATSDR	Agency for Toxic Substances and Disease Registry
BTU	British thermal unit
CAA	Clean Air Act
CARB	California Air Resources Board
CAS	Chemical Abstracts Service
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CNS	central nervous system
DOT	Department of Transportation
EH&S	Environmental Health & Safety
EPA	Environmental Protection Agency
ERP	Environmental Results Program
FDA	Food and Drug Administration
gal	gallon
GHS	Globally Harmonized System of Classification and Labelling of Chemicals
HAP	hazardous air pollutant
HC	hydrocarbon
IARC	International Agency for Research on Cancer
IWW	industrial wastewater
kg	kilogram(s)
kWh	kilowatt hours
L	liter
lb	pound
LD_{50}	lethal dose (to 50% of test population)
LDR	leak detection and repair
MassDEP	Massachusetts Department of Environmental Protection
MCL	maximum contaminant level
MCLG	maximum contaminant level goal
mg	milligram(s)
MSDS	Material Safety Data Sheet
NAAQS	National Ambient Air Quality Standards

NESHAP	National Emission Standard for Hazardous Air Pollutants
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
nPb	n-Propyl bromide
NTP	National Toxicology Program
OEHHA	Office of Environmental Health Hazard Assessment
OSHA	Occupational Safety and Health Administration
PCE	perchloroethylene
PEL	permissible exposure limit
perc	perchloroethylene
POTW	publicly owned treatment works
ppm	parts per million
psi	pounds per square inch
RCRA	Resource Recovery and Conservation Act
SNAP	Significant New Alternatives Policy
STEL	short-term exposure limit
TCE	trichloroethylene
TCLP	Toxicity Characteristic Leaching Procedure
TLV	threshold limit value
TUR	toxics use reduction
TURA	Toxics Use Reduction Act
TURI	Toxics Use Reduction Institute
TWA	time-weighted average
US	United States
USEPA	United States Environmental Protection Agency
VOC	volatile organic compound
µg	microgram(s)

I. Introduction: Alternatives to Perchloroethylene in Professional Garment Cleaning

Background

Perchloroethylene – also known as perc or PCE (the full name perchloroethylene and the abbreviation 'perc' will be used interchangeably throughout the document) – is a solvent that is used for cleaning garments. It is the solvent that has been most often used by professional dry cleaners. Perc has been the standard dry cleaning solvent because of its effectiveness, ease of use, and relatively low cost. However, improper use, storage and disposal of perc have resulted in widespread contamination of groundwater and soil at dry cleaning sites. Exposure to perc is also associated with a variety of adverse human health effects, especially in dry cleaning workers. Because of these impacts, perc is more strictly regulated today than in the past, and many cleaners are investigating alternatives for use in their operations.

In 1999, the United States Environmental Protection Agency estimated that 85% of professional garment care facilities in the United States used perc as their main cleaning solvent. Based on more recent informal industry surveys in 2009 and 2012, the estimate is significantly lower – between 50 and 70% (AmD 2009, AmD 2012a). According to these surveys, many US cleaners have switched to other solvents or cleaning methods, and are also increasingly using wet cleaning to do a significant portion of their cleaning volume (AmD 2012b). Even with these trends, Massachusetts dry cleaners reported using more than 450,000 pounds of perc and generating over 290,000 pounds of hazardous waste in 2010 (MassDEP ERP).

About This Report

This document has been prepared to:

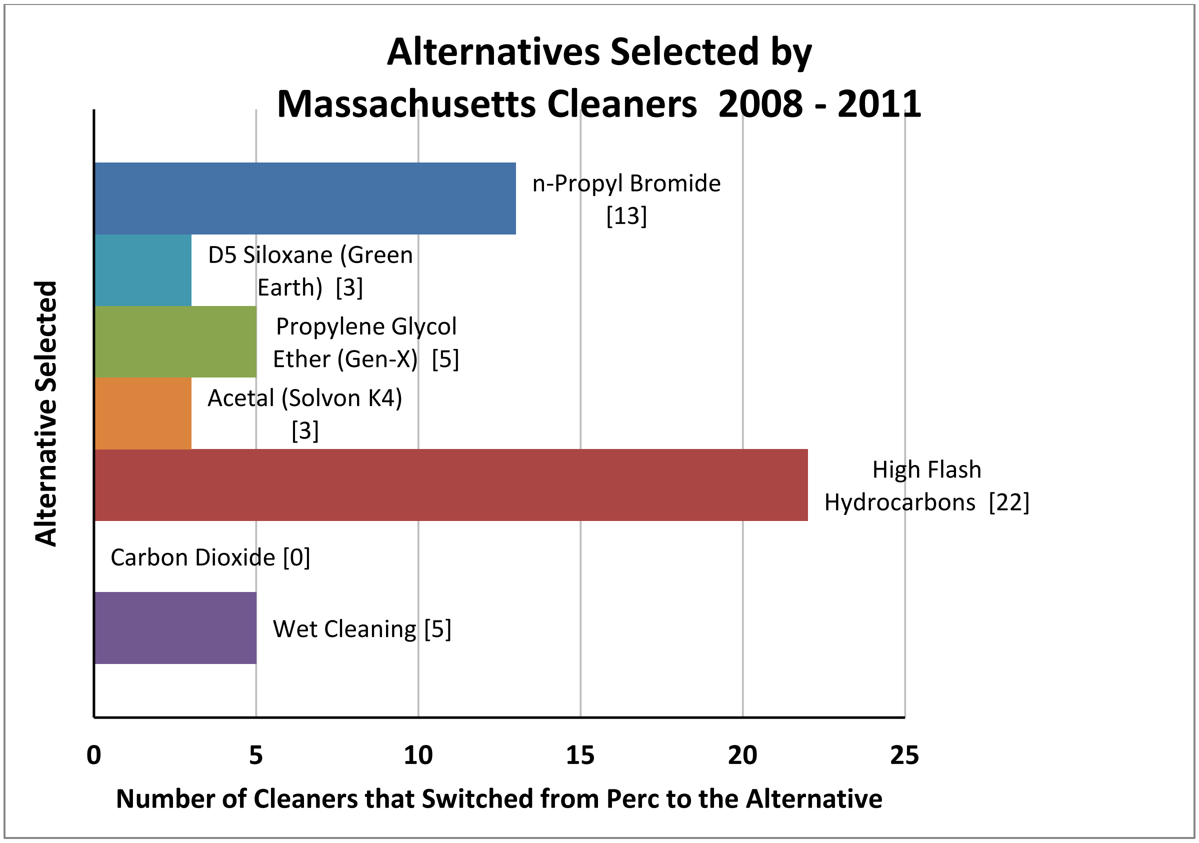
1) Provide background information about the use of perc in dry cleaning;
2) Provide technical, financial, environmental, health and safety, and regulatory information on alternatives to perc; and
3) Assist dry cleaners in the process of identifying which alternative(s) offer the best fit for their facility.

Information about perchloroethylene is provided in Section II of this report, and its alternatives in Section III, with a comparison of the alternatives to perc in Section IV.

About the Alternatives

The alternatives to perc that are assessed in this report were chosen based on national trends in dry cleaning, and on efforts under way in Massachusetts to find economically viable and environmentally preferred methods for professional garment cleaning.

To provide insight into trends in Massachusetts, the MassDEP's Environmental Results Program (ERP) data were analyzed (MassDEP ERP, Skogstrom 2012). Since 2008, over 50 cleaners reporting under the MA ERP program reported that they exited the program because they have eliminated the use of perc at their facility. These facilities report that they have moved to various alternatives as shown in the table below.



Note that this does not capture the cleaners in Massachusetts that are using alternative processes in addition to perc. For example, as mentioned previously, cleaners are increasingly adding wet cleaning to their suite of technologies.

The seven alternatives assessed are:

- Professional wet cleaning
- Liquid carbon dioxide
- High flash hydrocarbons
- Acetal
- Propylene glycol ethers
- Cyclic volatile methyl siloxane (D5)
- n-Propyl bromide (nPB)

Professional Wet Cleaning

Professional wet cleaning is a water-based cleaning process, which uses computer-controlled washers and dryers along with biodegradable detergents and specialized finishing equipment to process delicate garments that would otherwise be dry cleaned. Detergents used in wet cleaning are typically supplied by a detergent (or soap) supplier and injected into the washer through a computer-controlled and programmable pumping system. There are currently at least six dedicated wet cleaning facilities in Massachusetts, and many others who process some portion of their garments using wet cleaning.

Liquid Carbon Dioxide

Carbon dioxide (CO_2), as either a liquid or a supercritical fluid, can be used to clean garments in specialized equipment. The most common process uses liquid carbon dioxide at a pressure of 700 pounds per square inch and uses detergents specifically designed for this process. The CO_2 method of garment cleaning combines liquid carbon dioxide with cleaning agents in a traditional basket-style machine. Currently, this method is not in use in Massachusetts, and is not a widely available option in the US. Equipment is currently available from Cool Clean Technologies, Inc.

High Flash Hydrocarbons

High flash hydrocarbons are a class of low-odor petroleum-based dry cleaning solvents characterized by a flash point greater than 140^{o}F. This technology is the most widely used alternative to perc dry cleaning. The most common high flash point hydrocarbon solvent in use in Massachusetts is DF-2000^{TM}.

Acetal

Acetals are halogen-free combustible solvents. A new acetal-based dry cleaning solvent system came onto the US market in 2010, manufactured and distributed by Kreussler Inc. using the name Solvon K4. Solvon K4's main ingredient is 1-(butoxymethoxy) butane, also referred to as butylal or formaldehyde dibutyl acetal. Several Massachusetts cleaners have switched or are considering switching from perc to Solvon K4.

Propylene Glycol Ethers

Glycol ethers are a class of petroleum solvents that were introduced as an alternative to perc in dry cleaning in the late 1990s. Glycol ether systems can typically be used with a hydrocarbon machine after minor modifications. Several glycol ether systems have been commercially available, and several cleaners in Massachusetts reportedly use these systems.

Cyclic Volatile Methyl Siloxane

The current volatile methyl siloxane used in dry cleaning is the cyclic VMS decamethylcyclopentasiloxane (D5). Using D5 in dry cleaning is trademarked as the GreenEarth® dry cleaning system. It is an odorless, colorless liquid used in multi-solvent machines. GreenEarth® Cleaning claims that most 4th and 5th generation machines currently being used with hydrocarbons can be modified for use with D5. Many cleaners in Massachusetts use D5, though an exact number is not known.

n-Propyl Bromide (nPB)

N-Propyl bromide (nPB) is considered a "drop-in" replacement for perc in dry cleaning applications, which indicates that it can be used in existing (generation 3 or higher) perc dry cleaning equipment. nPB could be used in hydrocarbon equipment as well, although this would require more extensive modifications. Several cleaners in Massachusetts have switched or are considering switching their perc systems to nPB.

Assessing the Alternatives

There are numerous criteria to be considered when assessing the alternatives to perc in garment cleaning. This report evaluates the seven alternative cleaning methods based on the following factors:

- **Performance considerations**, including:

- Load capacity and cycle time. How many garments can be cleaned in a single load and how long does it take?
- Cleaning quality. Are garments cleaned thoroughly without being damaged?
- Garment compatibility. Are there any materials or types of garments that the cleaning fluids or equipment will damage or not clean thoroughly?
- Detergents and performance boosters. What detergents and other additives (such as softeners, sizers, conditioners, anti-static, anti-stain agents) are included in the vendor's solvent formulation, or can be added separately?
- Pre-treatment. Will the cleaning system require pre-treatment with spotting agents to remove stains or other soils before being processed? If spotting agents are needed, do they present their own environmental, health, or safety risks?
- Finishing requirements. Is additional equipment or processing needed following cleaning to restore the garment, such as final tensioning or extra pressing?
- Waste management. What waste management or hazardous waste considerations apply to the cleaning system?

- **Financial considerations**, including:
  - Financial investment. How much does new equipment cost? How much do the new chemistries cost?
  - How much does it cost to operate the equipment?
  - What are the typical costs for electricity to operate equipment, and for natural gas or oil to produce steam heat for drying, distillation and pressing?
- **Environmental and human health considerations**. Perc is bad for the environment and can be dangerous to use, but are the alternatives safer? Key criteria for environmental and human health for dry cleaning operations are provided.
- **Regulatory and safety considerations**. How do federal and Massachusetts regulations differ for alternative dry cleaning systems? Are there new regulatory concerns or physical safety issues (e.g., flammability) presented by the alternatives?

II. Description of Perchloroethylene Dry Cleaning

This section of the report provides base information on the most prevalently used solvent in the dry cleaning industry today. The information presented here is used as a baseline in this alternatives analysis to compare the seven alternatives to perc in the following two sections of the report.

Technical Information

Chemistries

Perchloroethylene (CAS No. 127-18-4) is a clear, colorless, non-flammable liquid with an ether-like odor. Its chemical formula is C_2Cl_4. Other names for perchloroethylene include perc, PCE, tetrachloroethylene, tetrachloroethene, ethylene tetrachloride, and carbon dichloride.

Equipment and Processes

Modern perchloroethylene dry cleaning equipment is complex machinery that washes clothes in the solvent, then spins them and dries them before they are removed for pressing. Fourth generation machines include a refrigerated condenser and carbon adsorption vapor recovery system and a filtration and distillation system to allow waste perc to be recovered and re-used (Grout & Sinsheimer 2004). Fifth generation systems also include a door lock to ensure that the machine is not opened prematurely.

Performance

Historically, perc has been the standard dry cleaning solvent because of its effectiveness, ease of use, and relatively low cost. Perc can clean a wide range of materials, though it can sometimes damage leather, suede, beaded garments or other delicate fabrics. It is an aggressive solvent, but is easy to use and is considered to be generally very “forgiving.” Aggressive pretreatment of spots is typically unnecessary when using perc, and once clean, garments are completely dry, and can then be finished using standard pressing equipment.

Waste Management

Waste perchloroethylene – including contaminated filters – is regulated as a hazardous waste by the USEPA and the Commonwealth of Massachusetts. Storage, transport and disposal of waste materials must be done in accordance with state and federal regulations.

Financial

A new 4^{th} generation perc machine can cost between $40,000 and $65,000, and in 2010 the cost of perc itself was $16.95 per gallon (NEFA 2010). Based on eight case study shops in California, the total cost per pound cleaned ranged from $0.63 to $1.94, averaging $1.02 (IRTA 2005). Operating costs have been estimated to be 26.6 kWh/100 lbs for electricity and 12 therms /100 lbs for natural gas use (Sinsheimer 2009).

Environmental, Health and Safety

While perc’s proficiency as a cleaner is undeniable, its toxicological footprint is also significant.

Environmental Impacts

Perc can be readily found in the environment because it is persistent in water, soils, air, and in sediments (USEPA PBT 2006, EU RA 2005). Bioaccumulation of perc in aquatic organisms is estimated to be low (USEPA PBT

2006). The aquatic toxicity of perc is considered moderate (HSDB 1982). Concentrations of perc in the environment tend to be higher in urban and industrial areas than in rural and suburban areas (ATSDR 1997). However, the public is not only exposed to perc due to environmental contamination but may also be exposed through the presence of residual perc in dry-cleaned garments and consumer products. Perc is a volatile organic compound (IAQ 2011), but is exempt from Clean Air Act National Ambient Air Quality Standards outdoor regulations due to negligible photochemical reactivity (USEPA 2009).

Health Effects

The Agency for Toxic Substances and Disease Registry (ATSDR) estimates that the most prevalent route of exposure to perc is by inhalation, though exposure can also occur orally through ingestion of contaminated water or food (ATSDR 1997). Perc inhaled by pregnant women can reach a developing fetus and has been found in the breast milk of mothers exposed to the chemical (ATSDR 1997). Dermal exposure is less likely, but when exposed, irritation or blistering can occur. Most notably, regardless of the route of exposure, perc can damage the body's central nervous system and the liver (ATSDR 1997). Perc is a known dermal, ocular and respiratory irritant (NIOSH 2004).

Effects of chronic exposure to perc include dizziness, impaired judgment and perception, damage to the liver and kidneys, and respiratory disease (NIOSH 2004), as well as immune and hematologic system effects (USEPA 2012). A study of dry cleaning workers also showed an association between perc exposure and hypertensive end-stage renal disease (Calvert 2010). The oral LD_{50} value in rats is 2,629 mg/kg (ChemID). Other risks include neurotoxicity and reproductive and developmental toxicity (USEPA 2012). Perc has been classified as a "probable human carcinogen" by the International Agency for Research on Cancer (IARC 1995) and by the U.S. Environmental Protection Agency as "likely to be carcinogenic to humans" (USEPA 2012).

Table 1. Summary of Health Effects Associated with Perc

Acute Effects (Short Term)	**Chronic Effects** (Long Term)	**Cancer Hazards**
• Single exposures can cause central nervous system effects (dizziness, headache, sleepiness, confusion, and nausea) and difficulty speaking or walking. • High-level exposure may cause vomiting, unconsciousness and death. • May cause skin irritation. • Irritating to the eyes, causing pain, redness and general inflammation. • Irritating to the nose and throat.	• Long-term exposure may cause liver and kidney damage. • Prolonged and repeated dermal exposure may cause dermatitis. • Increased health risks for people with pre-existing skin disorders and impaired renal or liver function. • Exposure may lead to developmental or reproductive toxicity. • Immune and hematologic system effects.	• IARC Group 2A, probable human carcinogen. • Reasonably anticipated to be a human carcinogen, (as evidenced by animal testing) by the US National Toxicology Program (NTP 2011a). Animal testing has linked high exposure to liver and kidney cancer as well as leukemia. • Studies of occupational exposure to perc in dry cleaning environments indicate an increased risk of kidney cancer for workers. • USEPA notes perc is "likely to be carcinogenic to humans" by all routes of exposure.

Regulatory

Perc-based dry cleaning is now subject to increased regulation by a wide range of federal, state, regional, and local agencies. Perc is listed as a hazardous air pollutant under the Clean Air Act and its use at dry cleaning facilities is regulated by the National Emission Standard for Hazardous Air Pollutants (NESHAP), which limits emissions of perc from existing and new dry cleaning facilities (USEPA 2005). Dry cleaning plants using more than 2,100 gallons of perc annually are considered major sources and must comply with the federal NESHAP; plants using less than 2,100 gallons/year are considered area sources and are regulated in Massachusetts under the multi-media MassDEP Environmental Results Program (ERP) for Dry Cleaners.

NESHAP requires that all existing facilities implement leak detection and repair (LDR) programs and prohibits the use of existing transfer machines. These requirements are intended to minimize the potential release of perc into the atmosphere, or spills of perc that could enter the environment. In new facilities, an LDR program must be implemented that includes the use of non-vented dry-to-dry machines with refrigerated condensers and secondary carbon adsorbers (USEPA 2006). Operating and maintenance practices associated with LDR address the machine itself, auxiliary equipment (such as filters, water separators and distillation units), control devices, and general housekeeping. A halogenated hydrocarbon detector must be used weekly and weekly checks for perceptible leaks must be conducted for all perc dry cleaners (MassDEP 2008).

Because of ongoing concern about worker and public health risks, environmental contamination, and the increasing availability of alternatives, the Massachusetts Toxics Use Reduction Administrative Council designated perc as a Higher Hazard Substance in 2009. This designation lowered the reporting threshold to 1,000 lbs of annual use. Any facility that uses over 1,000 pounds (or approximately 75 gallons) of perc within a calendar year and has at least 10 full time equivalent employees must report its use of perc by July 1 of the following year. These facilities must also develop a toxics use reduction (TUR) plan, which consists of examining options for reducing the use of perc. In addition, the MassDEP is requiring the elimination of perc machines in co-residential shops and shops that are co-located with other "sensitive receptors" (e.g., day care centers, health care facilities, schools, pre-schools and youth/senior centers) by 2020.

The American Conference of Governmental Industrial Hygienists recommends, for perc exposure, a time-weighted average - threshold limit value (TWA-TLV) of 25 ppm and a short-term exposure limit (STEL) of 100 ppm for a 15-minute TWA (ACGIH 2006). OSHA has a mandatory 8-hour TWA permissible exposure limit (PEL) of 100 ppm.

Table 2 summarizes environmental regulations pertaining to the use of perc in dry cleaning.

Table 2. Massachusetts and Federal Regulations Pertaining to Perc Use in Dry Cleaning

Massachusetts Agency	Regulation and Requirements
DEP (Department of Environmental Protection)	
Toxics Use Reduction Act (TURA)	Perc is listed as a toxic substance under TURA, and has been designated as a higher hazard substance. Facilities using more than 1,000 lbs perc/year and having more than 10 full time employees must report on their use annually and prepare a toxics use reduction plan every other year.
Environmental Results Program (ERP) for Dry Cleaners 310 CMR 7.26(10)-(16)	Dry cleaners using perc are required to comply with the ERP, which mandates annual self-reporting on air emissions controls, wastewater disposal practices, and hazardous waste management associated with the use of perc in their operations.

US Federal Agency	Regulation and Requirements
EPA (Environmental Protection Agency)	
Clean Air Act	Listed as a Hazardous Air Pollutant (HAP).
	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: Listed as a Priority Pollutant. 0.69 µg/L based on human health, fish/shellfish and water consumption, 3.3 µg/L based on human health, fish/shellfish consumption
Emergency Planning and Community Right-to-Know Act	CERCLA Reportable Quantity for spills and accidental releases is 100 lbs.
	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 perc include U210, F001, F002, F024, F025, K016, K019, K020, K073, K116, K150, K151.
	Characteristic Toxic Hazardous Waste: TCLP Threshold = 0.7 mg/L (D039)
Safe Drinking Water Act	Maximum Contaminant Level (MCL) = 0.005 mg/L Maximum Contaminant Level Goal (MCLG) = zero
OSHA (Occupational Safety and Health Administration)	
Permissible exposure limit	Time-weighted average (8 hr) = 100 ppm
DOT (Department of Transportation)	
Code of Federal Regulations Title 49, Part 172	Considered a hazardous material and a marine pollutant. Special requirements have been set for marking, labeling, and transporting this material.
FDA (Food and Drug Administration)	
Code of Federal Regulations Title 21, Part 165.110	Maximum permissible level in bottled water = 0.005 mg/L

III. Description of Alternatives for Professional Garment Cleaning

Introduction

In 2009 and 2012 *American Drycleaner* magazine identified several alternative dry cleaning solvents and processes being used, based on informal national surveys of US dry cleaners (AmD 2009, AmD 2012a). This survey showed that the most widely used alternatives to perc in dry cleaning are high flash point hydrocarbon systems. Though less popular than hydrocarbon systems, other alternatives include systems that use cyclic volatile methyl siloxanes or glycol ethers as the base solvent.

Similar to the *American Drycleaner* survey results, dry cleaners in Massachusetts not using perc have largely chosen high flash point hydrocarbons (e.g., DF 2000™) as a replacement, but glycol ethers (e.g., Gen-X), volatile methyl siloxane (Green Earth®), and wet cleaning are also in use. Many facilities also make use of more than one cleaning technology to suit their cleaning needs. A new solvent sold under the brand name Solvon K4, in the chemical category of acetals and similar in operation to hydrocarbon systems, is also beginning to be used in the region, and has been included in this report for comparison with other perc alternatives. Liquid carbon dioxide is not currently being used in Massachusetts (NEFA 2011), and several cleaners in Massachusetts have switched or are considering switching their perc systems to nPB. Low flash hydrocarbons (HCs) with flash points below 140°F (e.g., Shellsol D40) are infrequently used, and have largely been replaced by high flash hydrocarbons. Therefore, low flash HCs have not been evaluated in this alternatives assessment.

This section provides detailed descriptions of seven alternatives to perchloroethylene for professional garment cleaning:

- Professional wet cleaning
- Liquid carbon dioxide
- High flash hydrocarbons
- Acetal
- Propylene glycol ethers
- Cyclic volatile methyl siloxane (D5)
- n-Propyl bromide (nPB)

Like the description of perchloroethylene in Section II, each alternative is described in terms of technical, financial, environmental, health and safety, and regulatory factors.

Table 3 below summarizes the alternatives to perc that are on the market today and lists the trade names of products they are associated with. The following sections of the report go into further detail on each of these alternatives categories. See Appendix A for additional information on the solvent ingredients.

Table 3. Dry Cleaning Solvent Categories and Associated Trade Names

Category	Trade names
Perc	
nPB	Drysolv® Fabrisolv ™ XL
High flash hydrocarbons	DF2000™ Fluid EcoSolv® (Chevron Phillips) ShellSol D60 PureDry Caled Hydroclene
Cyclic VMS - D5	Green Earth® - D5 solvent provided by Dow Corning, GE, Shin-Etsu, or other chemical manufacturer
Propylene glycol ethers	Solvair® Rynex 3® Impress® Gen-X
Acetal	Solvon K4
Liquid CO2	Cool Clean Technologies, Solvair®
Supplemental water-based technology	GreenJet™
Wet cleaning	Several manufacturers provide washers, dryers, tensioning equipment and detergents. Equipment manufacturers include Wascomat, Miele, Continental Girbau, HwaSung, and AquaSolo.

Wet Cleaning

Technical Information

Professional wet cleaning is a water-based cleaning process, which uses computer-controlled washers and dryers along with biodegradable detergents and specialized finishing equipment to process delicate garments that would otherwise be dry cleaned. Professional wet cleaning technology has improved since its inception and has been demonstrated to be a technically viable and commercially feasible substitute for perc dry cleaning.

Professional wet cleaning is used by many garment cleaners in Massachusetts for all or some percentage of garments or when requested by customers. It is uncertain exactly how many offer professional wet cleaning services, as that information is not captured under any regulatory program. There are now at least six garment cleaners in Massachusetts that use wet cleaning exclusively.

Chemistries

The solvent used in wet cleaning systems is water. Therefore, in comparing perc and other organic solvents to wet cleaning, water is less toxic and less costly, but also less effective without the use of detergents and additives. Because wet cleaning relies more heavily on the detergents for effectiveness than other dry cleaning systems, this assessment will examine the detergents used in professional wet cleaning. However, it should be noted that many of these same detergents and additives are also used in other dry cleaning technologies, and while they are used in slightly greater percentages for wet cleaning, the impact on health and the environment will be similar for all alternatives, including perc.

Detergents used in wet cleaning are typically supplied by a detergent (or soap) supplier and injected into the washer through a computer-controlled and programmable pumping system.

The following analysis was based on three Kreussler professional wet cleaning products (Lanadol Aktiv, Lanadol Apret, and Lanadol Avant)[1]. Kreussler bases its primary detergent (Lanadol Aktiv) on a collagen-based surfactant. Other chemicals found in the various professional wet cleaning Kreussler products include: branched and linear alcohol ethoxylates (CAS # 106232-83-1); oleic acid monoethanolamid, ethoxylated (CAS # 26027-37-2); alcohols C12-C18 ethoxylated, propoxylated (CAS # 69227-21-0); 2-(2-butoxyethoxy)ethanol (CAS # 112-34-5); sodium laurylglutamate (CAS # 29923-31-7); glycine, N-(2-[(2-hydroxyethyl)amino]ethyl), N'-Cokos-acyl derivates, mono sodium salts (CAS # 61791-32-0); proprietary organic solvents and perfumes. The CAS #'s indicated above were used in the environmental health and safety evaluation of wet cleaning detergents and additives, and are assumed to be representative of products on the market.

Equipment and Processes

Professional wet clean washers use a computer to control the rotation of the cleaning drum in order to minimize agitation while providing sufficient movement for effective garment cleaning. Wet clean washers are also equipped with a computer-programmed detergent injection system, which allows the operator to specify the amount and type of wet clean detergent and other boosters and additives used for each load through programmed cycles. Wet clean dryers include a computer-controlled residual moisture sensor to ensure that

[1] Information was requested from two major distributors of wet cleaning chemistries in Massachusetts: Adco and Kreussler. The Adco information provided was not sufficiently detailed to use for this assessment.

garments retain a proper amount of moisture after the dry cycle is complete. This is necessary to avoid over-drying of garments, thereby eliminating shrinkage.

Wet cleaned garments are finished using specialized tensioning equipment. There are two main types of tensioning equipment: form finishers and pants toppers. Both pieces of equipment function by using steam to relax fibers, moving parts to stretch and shape clothes, and hot air to dry. Tensioning presses are designed to reverse or prevent shrinkage and/or seam crumbling and creasing of garments by applying widthwise and lengthwise tension on garments during the pressing process. Tensioning equipment is an essential component of the wet cleaning process. Tensioning equipment has been shown to reduce the pressing labor time at professional wet cleaning facilities.

Performance

Performance of wet cleaning technology is optimized when proper wet cleaning equipment is used and when operators receive adequate training on the washer and dryer programs and tensioning equipment. Dimensional change (shrinking and stretching) of wet cleaned garments is only a concern if the cleaner does not use tensioning equipment or uses it incorrectly.

In February 2007, the Professional Wet Cleaning Demonstration Project completed through the Occidental College Urban and Environmental Policy Institute published their results of a study of seven cleaners who converted to dedicated wet cleaning sites. The study evaluated each cleaner's operations as a perc dry cleaner and used those results as a benchmark for comparison in the evaluation of each cleaner's operations as a professional wet cleaner. Five of the seven cleaners were able to professionally wet clean 99% of garments brought in by customers. Cleaners noted that their send-outs were due primarily to oil-based stains. Customer retention rates reported by demonstration site cleaners ranged between 98% and 100% (Sinsheimer 2007).

Between 2009 and 2011, the Massachusetts Toxics Use Reduction Institute assisted three Massachusetts dry cleaners in converting their operations to dedicated wet cleaning facilities. According to these facilities, once employees were fully trained, they experienced no increased send-outs, redos, or damage claims. These facilities have, however, sent out certain fur, leather, and suede items (Onasch 2010).

An additional performance metric for garment cleaning is the brightness of colors. It has been noted by cleaners in both California and Massachusetts that the wet cleaning process leads to brighter colors and whiter whites. This is likely due to the absence of recycled solvent, which can cause dinginess in the garments.

Waste Management

Wastewater generated from the wet cleaning process is considered industrial wastewater (IWW), and does not require management as a hazardous waste. Wet cleaning operations in Massachusetts, as for laundry operations, must adhere to the state's IWW regulations (310 CMR 72), which require one of the following options:

1. Discharge to sewer/publicly owned treatment works (POTW). Cleaners must comply with MassDEP sewer discharge regulations (314 CMR 7.05[2][g]). This typically requires a discharge agreement with the POTW, which may include limitations on the amount of oils and grease, suspended solids and/or pH in the wastewater.

2. Discharge to an industrial wastewater holding tank, complying with applicable regulations (310 CMR 72.04 [5])
3. Discharge to groundwater, surface water or septic system. A discharge permit is required. However, applying for and obtaining such a permit is costly and time intensive.

Financial

The costs for a wet cleaning system range significantly depending on the brand, the size needed for the throughput of the shop, and whether the cleaner already has appropriate finishing equipment in-house.

At least one line of wet cleaning equipment is sold as a set – including a washer and dryer – that ranges in price from $23,000 to $34,000. Generally, however, the equipment is sold as individual pieces. An equipment report published in 2007 included these cost ranges (UEPI 2007):

- Washers: $10,000 - $25,000 (capacities of 20 to 85 pounds)
- Dryers: $4,000 - $5,000 (capacities of 30 to 75 pounds)
- Pants finishers: approximately $10,000
- Shirt/blouse finishers: - $11,000 - $19,000
- Dispensing systems - $1,000 - $2,000

Therefore, total costs range from $36,000 to $61,000. This is consistent with data from three cleaners that TURI has worked with to purchase wet cleaning equipment, who have spent an average of $52,000 for the five main pieces of wet cleaning equipment.

The costs of detergents have been estimated to fall within the range of $25-$31/gallon (Fitzpatrick 2011). Based on four case study shops in California, total cost per pound cleaned ranged from $0.57 to $1.32, averaging $1.10 (IRTA 2005).

Studies in California and Massachusetts have shown that electricity use is reduced up to 60% and natural gas use may be reduced up to 20% (Sinsheimer 2004 and Onasch 2010). This drop in energy use can most likely be attributed to the elimination of an energy-intensive solvent recovery system; this energy use reduction is only seen in facilities dedicated to wet cleaning, as a shop also using a solvent would still be using the recovery system. In 2009, electricity use was estimated at 9.3 kWh/100lbs and natural gas at 9 therms/100 lbs (Sinsheimer 2009). Facilities may also see a drop in water use when they convert to dedicated wet cleaning due to the elimination of condensing/chilling operations associated with a solvent process (Onasch 2010). Newer wet cleaning equipment also uses less water than traditional laundry machines, so if a facility shifts to using their wet cleaning equipment more than their laundry equipment, they may also see a drop in water use.

Environmental, Health and Safety

There is no hazard associated with the primary solvent in wet cleaning, water, but it is important to examine the detergents and other additives used in the process.

Environmental Impacts

Based on the review of safety data sheets associated with detergents and surfactants in Kreussler products and other information available for the various additives associated with wet cleaning systems, the only concern appears to be moderate persistence in sediment (USEPA PBT 2006). One additive exhibits moderate aquatic toxicity, but is readily biodegradable (USEPA PBT 2006, Akzo 2009). Each of the additives that could be evaluated using the US Environmental Protection Agency's tool, the PBT Profiler, exhibits low bioaccumulation values (USEPA PBT 2006).

Health Effects

A review of the same Kreussler data sheets indicates a risk of skin irritation and eye damage (Akzo 2009, Aktiv 2009, Avant 2009). None of the components of the additives evaluated have been classified by IARC as possible carcinogens. One component found in one product in amounts ranging from 1% to 5% by weight is a butoxy ethanol, a glycol ether, which may be associated with potential anemia, reproductive toxicity, and effects on the central nervous system (CNS), liver, and kidneys (HAZMAP 2011). During use in the washer, the concentration of butoxy ethanol in the solvent (water) is approximately 0.1%, below the 1% level considered de minimis for non-carcinogens in a formulation. Nevertheless, detergent manufacturers and dry cleaners should check products for the presence of this ingredient, and avoid exposure where possible. It is a likely ingredient in detergent and additive packages for all solvent types.

Safety Concerns

There are no known safety concerns associated with wet cleaning processes. Only one component of one product present in quantities ranging from 1% to 5% is a VOC under EPA's National Ambient Air Quality Standards (NAAQS) definition (USEPA 2009). The Kreussler formulations range from a pH of 3.4 to 11.2.

Regulatory

There are no occupational exposure or hazardous waste regulatory requirements for the wet cleaning system. However, wastewater from wet cleaning is considered industrial wastewater, and must be discharged to a sewer or a wastewater holding tank. All industrial wastewater is currently prohibited from discharge to septic systems in Massachusetts without obtaining a groundwater discharge permit, which is a costly and time-intensive process. Wet cleaning facilities on sewers typically develop discharge agreements with their publically owned treatment works which may include limitations on the amount of oils and grease, suspended solids and/or pH in the wastewater.

Carbon Dioxide (CO_2)

Technical Information

Carbon dioxide, as either a liquid or a supercritical fluid, can be used to clean garments in specialized equipment. The more common process uses liquid carbon dioxide at a pressure of 700 pounds per square inch and uses detergents specifically designed for this process.

The CO_2 method of garment cleaning combines liquid carbon dioxide with cleaning agents in a high-pressure basket-style machine. It is similar to today's front-load, mechanical-action machines, and features wash and extract cycles. A detergent system adds to the cleaning ability of the liquid CO_2. After the cleaning cycle, the machine pulls the mixture of liquid CO_2 and cleaning agents away from the clothes under vacuum, then filters and reuses the solution (DfE CO2 1999).

Because of the pressure required, CO_2 equipment is more expensive and costly to maintain than perc equipment. 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, but there are some machines that are about the same size as a traditional perc machine (Morris and Wolf 2005).

Currently, there are no known users of CO_2 dry cleaning equipment in Massachusetts and it is not a widely available option in the US. CO_2 equipment is currently available from Cool Clean Technologies, Inc.

Chemistries

Liquid CO_2 (CAS # 124-38-9), the solvent used in dry cleaning, is pressurized (approximately 700 psi), non-flammable CO_2. The cleaning agents used in one system are proprietary but, according to the USEPA Design for Environment (DfE) program, are reported to be recyclable (DfE CO2 1999). The Solvair® system uses propylene glycol ether solvents combined with liquid CO_2; this system is covered in the glycol ether section of this report.

Equipment and Processes

The first carbon dioxide (CO_2) cleaning systems were introduced in 1999 by Micell Technologies, Inc.; these systems use high pressure so that the CO_2 is in liquid form. There were approximately 40 to 50 CO_2 retail dry cleaning systems operating in the US in 2007 (DLI 2007). The cycle time for CO_2 cleaning is 35 to 45 minutes, using a 60-pound capacity system (DfE CO2 1999). A current manufacturer of CO_2 equipment for sale in the US is Cool Clean Technologies, Inc.

Performance

Carbon dioxide-based cleaning is said to cause less fading and wear on clothing when compared with traditional dry cleaning. Because it does not require heat to clean, the process is also gentler on clothes (DfE CO2 1999). Some reports indicate that, because of the low solvency of CO_2, more spotting is required to achieve acceptable cleaning results (DLI 2007). However, any stains that remain on the garments are not heat set by this process and therefore post-spotting is reported to be very effective. In addition, CO_2 systems are reported to provide better colorfastness than perc. The CO_2 system is not compatible with triacetates and some acetates with specific dispersive dyes, yellow in particular (DfE CO2 1999).

Waste Management

Because liquefied CO_2 under high pressure will immediately evaporate if there is any type of leak in the machine, it is unlikely that a CO_2 release would result in soil or water contamination. Soils, including pre-spotting chemicals added before garments are cleaned, are removed from garments with other soils and are captured in the filtration system. The CO_2 system does not result in the generation of waste solids or wastewater that would be classified as hazardous or that would require special treatment.

Financial

Because CO_2 machines operate at high pressure levels, the machines are classified as high-pressure vessels, and are consequently relatively expensive, ranging typically from $100,000 to $150,000 (DLI 2007). A 2005 study prepared for the California Air Resources Board estimates that the annualized cost per pound of garments cleaned in a large facility that uses CO_2 is $1.40/lb (IRTA 2005). The USEPA DfE program reports that operating costs are estimated to be competitive with conventional dry cleaning technologies (DfE CO2 1999). The estimated electricity usage has been noted as 30.9 kWh/100lbs clothing cleaned (Sinsheimer 2009). Purchase of CO_2 and added detergents has been reported at $0.18/lb CO_2 and $40/gal of associated detergent (IRTA 2005).

Environmental, Health and Safety

Environmental Impact

Carbon dioxide is not persistent in soil, and is a natural component of our atmosphere. While CO_2 is known to be a greenhouse 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 the use of such a system does not contribute to global warming overall (CARB 2008). CO_2 is not a volatile organic compound.

Health Effects

The recommended exposure limit for carbon dioxide from the National Institute for Occupational Safety and Health (NIOSH) is 5000 ppm (NIOSH 2004). In sufficient concentrations, carbon dioxide is an asphyxiant. Release of CO_2 into an enclosed, unventilated space could thus be a concern. High concentrations of carbon dioxide can affect the respiratory system, cardiovascular system, lungs, skin and central nervous system. Dermal and/or ocular exposure to liquid could result in frostbite (NIOSH 2004). CO_2 has not been classified by IARC as a possible carcinogen.

Safety Concerns

Carbon dioxide must be kept under pressure to remain in liquid form; the pressure required for carbon dioxide is similar to that required for other gasses commonly used in industry. Pressurized gasses pose a safety hazard if proper equipment is not used; careful attention to operating procedures is required.

Regulatory

There are no regulatory restrictions associated with liquefied CO_2 as a dry cleaning solvent, either at the federal level or the state level. There are, however, safety regulations pertaining to the use of pressurized vessels. Equipment associated with this technology must be constructed in accordance with American Society of

Mechanical Engineers (ASME) codes, and all pressurized tanks should be stored and managed to prevent releases in accordance with ASME's Boiler and Pressure Vessel code, as referenced in Massachusetts regulation 527 CMR 49.00. The OSHA permissible exposure limit for carbon dioxide is 5000 ppm (NIOSH 2004).

High Flash Hydrocarbons

High flash hydrocarbons are a class of petroleum-based dry cleaning solvents characterized by an ignition temperature, if exposed to flame, greater than 140°F. This technology is the most widely used alternative to perc dry cleaning. Prior to the 1950s, low flash point petroleum hydrocarbons, such as Stoddard Solvent, were used for dry cleaning, but because of fire concerns, they were replaced by non-flammable perchloroethylene in the 1950s. However, in recent years, new higher flash point synthetic paraffinic hydrocarbons with low odor have been introduced to the market, and have been received well.

The most common high flash point hydrocarbon solvent in use in Massachusetts is DF-2000™ (Exxon/Mobil). Most other products are similar to DF-2000™, with the exception of PureDry, which contains up to 5% fluorinated compounds and has a significantly higher flash point of 350°F (CARB 2006). The review in this report is based on the primary ingredients in DF-2000™ (Exxon/Mobil) and Ecosolv® (Chevron Phillips). It is unclear whether PureDry is still commercially available.

Technical Information

Hydrocarbon systems need to continuously remove water and oils in order to avoid bacterial growth. Distillation systems may be used. One filter system with Tonsil® (a blend of activated calcium bentonite and diatomaceous earth) has demonstrated good performance.

Chemistries

DF-2000™ is a hydrotreated heavy naphtha-based petroleum product. This synthetic isoparaffinic substance is a combustible liquid, and is considered a hazardous material in accordance with OSHA 29 CFR 1910.1200 (EM 2010). The following CAS numbers were used for the environmental health and safety assessment: 68551-17-7 (C10-13 Isoparaffin) (Chevron 2011) and 64742-48-9 (Naphtha [petroleum], hydrotreated heavy) (EM 2010).

Equipment and Process

Some hydrocarbon (HC) machines are equipped with a refrigerated condenser (for vapor recovery) while others are not, and distillation is done in a vacuum. Initial cycle times of HC machines are longer than they are for perc; however, manufacturers have been working on reducing the process times to match those for perc. The typical hydrocarbon system has a total cycle time of 60 to 75 minutes and a load capacity ranging from 35 to 90 pounds. Storage tanks should be bottom drained often, and cleaners are advised to distill the solvent frequently to remove impurities (Morris and Wolf 2005).

One issue with the HC solvent is bacterial growth in the system. Keeping these systems free of water is therefore essential. The control of water can be accomplished by filtering the solvent through an absorbent material. In studies conducted in California, this process was found to also eliminate the need for distillation and reduce the need to add detergents during cleaning (Morris and Wolf 2005).

Performance

Hydrocarbon formulations are typically less aggressive on garments than perc. DF 2000™ is reported to be effective on delicates, and provides good "hand" (IRTA 2005).

Waste Management

Under the federal hazardous waste regulations, solid waste (such as cartridge filters) from HC systems would not be considered hazardous waste, and liquid waste (such as still residue) would only be a characteristic hazardous waste if it had a flash point below 140°F. Because state hazardous waste programs can be more stringent than the federal program, the final determination of whether waste regulations apply to HC systems should be based on the constituents of the product in use. Questions about the management of specific waste streams can always be addressed by the Business Compliance Division of MassDEP (go to http://www.mass.gov/dep/recycle/complian.htm to learn more, or contact Paul Reilly at 617-556-1097).

Cleaners should also consider whether or not their spotting chemicals generate hazardous waste. Based on RCRA (Resource Recovery and Conservation Act) regulations, certain solvents in excess of 10% in a product may render waste spotting chemicals a listed hazardous waste; cleaners should check with their waste hauler for appropriate identification. Waste spotting chemicals may also exhibit a hazardous waste characteristic. Testing of sample wastes from hydrocarbon dry cleaning facilities in California found perc and TCE in some separator water and sludge waste streams; it was suspected that the perc and TCE originated with spotting chemicals (IRTA 2005a).

In Massachusetts, waste high flash hydrocarbons must be managed as waste oil (see regulatory section).

Financial

Because of the fire suppression and oxygen sensor systems that are typically required by fire code for an HC system, the system costs can range from $38,000 to $75,000 (LA 2004). The costs of hydrocarbon solvent in California were reported in 2005 to be approximately $16/gallon (IRTA 2005), and from an on-line supplier to be $14 - $17/gallon (FabriClean 2012). Based on two case study shops in California, the total cost per pound cleaned ranged from $0.73 to $1.02, averaging $0.88 (IRTA 2005). The electricity use was estimated at 35.5 kWh/100 lbs and natural gas usage at 13.1 therms /1500 lbs (Sinsheimer 2009).

Environmental, Health and Safety

Specific ingredients in hydrocarbon solvents are often kept confidential, or ingredients are referred to on Material Safety Data Sheets (MSDS's) as a chemical class or family. This assessment is based on the main constituents of common products.

Environmental Impacts

High flash hydrocarbons have the capacity to persist and bioaccumulate in an ecosystem. These substances are estimated to be moderately persistent in sediment (USEPA PBT 2006). They are also expected to be highly toxic to the aquatic environment (USEPA PBT 2006). High flash hydrocarbons are VOC's with a boiling point in the range of 357-408°F.

Health Effects

Hydrocarbons are petroleum-based and can cause headaches, dizziness, nausea, and vomiting. The MSDS for DF-2000™ states that care must be taken to ensure that garments are completely dry before being worn, and notes that any solvent "not totally removed from absorbent clothing (e.g., shoulder pads, waist bands, etc.) that remains in contact with the skin for prolonged periods may cause skin irritation including redness, swelling and possibly blistering" (EM 2010). It is also indicated as an ocular and respiratory irritant (Chevron 2011). Animal studies indicate potential concerns for kidneys (Chevron 2011). High flash hydrocarbons are considered CNS toxicants (OEHHA 2010). These substances have not been classified for carcinogenicity by IARC.

In the absence of established exposure limits for these specific hydrocarbons, it is recommended that the ACGIH TWA-TLV of 100 ppm for Stoddard Solvent be used.

Safety Concerns

High flash hydrocarbons are less flammable than standard hydrocarbon solvents, such as Stoddard Solvent, but are still classified as combustible liquids. Handling of this solvent requires extra caution, such as provision of electrical grounds and bonding to minimize risk of static accumulation which could result in dangerous conditions (EM 2010). There is also a fire safety concern with the high flash hydrocarbons. Massachusetts Fire Prevention Regulations 527 CMR 3 adopts by reference National Fire Protection Association (NFPA) code 32 (NFPA 32). These materials are classified as Class IIIA solvents, which under NFPA 32 require a sprinkler system if the quantity of material in the machine and in storage is more than 330 gallons.

Regulatory

Waste high flash hydrocarbons are regulated at the state level as waste oil and must follow waste oil disposal requirements.

The Massachusetts Department of Fire Services regulates dry cleaning plants using Class IIIA solvents (those with flash points between 140°F and 200°F) in accordance with NFPA 32 as noted above. In addition, dry cleaners using combustible solvents should check with their local fire department to determine applicability of Massachusetts process safety management regulations 527 CMR 33 (MADFS).

Acetal

Technical Information

A new acetal-based dry cleaning solvent system came on to the US market in 2010, manufactured and distributed by Kreussler Inc. using the name Solvon K4. The Kreussler Company is a long-time producer of detergents and additives for the wet cleaning and dry cleaning industry. The Solvon K4 system includes a detergent concentrate (CLIPK4), a brushing agent (PRENETTK4) and a water and stain repellant agent (VINOYK4), in addition to the acetal solvent. The information provided in this section is largely based on interviews with dry cleaners in New England who have been using the acetal system for several months, as well as the manufacturer. There is growing interest in Massachusetts and the New England region in the acetal system. Interviews with some of the current users indicate that by and large they are happy with its performance.

Chemistries

Solvon K4's main ingredient (over 99%) is 1-(butoxymethoxy) butane (CAS # 2568-90-3), also referred to as butylal, dibutoxymethane or formaldehyde dibutyl acetal. Acetals are halogen-free combustible solvents.

Equipment

While new equipment can be purchased from the manufacturer for approximately $75,000, butylal can apparently also be used in hydrocarbon machines after adjusting the cycle time to 60-65 minutes. Machines designed specifically for butylal range in size from 40- to 90-pound load sizes. After a load is cleaned and dried, garments are finished on standard equipment.

Performance

Dry cleaners using the acetal solvent report that it cleans a variety of fabrics and garments effectively, and that it is more forgiving than perc when clothes have a lot of moisture in them. Clothes with glued-on decorations such as appliqués can be damaged with the solvent, as is sometimes the case with perc. Dry cleaners also report that butylal may require less spot pretreatment than perc. Some workers have found the solvent odor, described as sweet or fruity, objectionable.

Waste Management

Waste acetal solvent is considered industrial waste rather than hazardous waste and can be disposed of through standard industrial waste practices. However, because MassDEP has not reviewed the toxicity of this new dry cleaning substance, precautionary measures, such as notifying the wastewater treatment facility of this discharge, are recommended.

Financial

For dry cleaners currently using hydrocarbon equipment, switching to an acetal requires minimal investment. Dry cleaners currently using the system estimate that it costs approximately $4,000 to fill a converted hydrocarbon machine with solvent, and that operating costs are similar to the costs they experienced using their previous system. Dry cleaners not already using a hydrocarbon machine should expect a more significant investment. New equipment is estimated to cost between $50,000 and $100,000 (Fitzpatrick 2011). For example, a 60-pound machine cost $68,000 in 2011. This cost could be adjusted proportionally depending on the size of the machine. Operating costs associated with butylal are assumed to be similar to the operating costs of hydrocarbon systems, based on information from users and the maker of the solvent. The maker of the acetal solvent has noted that the natural gas or oil needed to make steam heat for solvent distillation in an acetal system is one quarter the BTU requirement of a hydrocarbon system and half the BTU requirement of a perc system. Because acetals are combustible, equipment will need to be fitted with fire suppression systems, similar to the requirements of hydrocarbon systems. The cost of Solvon K4 is currently estimated at approximately $28/gallon (Fitzpatrick 2011) to $34/gallon (Fabriclean 2012).

Environmental, Health and Safety

Much of the material provided in this section is based on information provided by the acetal system manufacturer or modeling results (e.g., USEPA's PBT profiler).

Environmental Impacts

Because the acetal solvent is relatively new to the market, environmental health and safety information for US audiences is very limited. Models of the persistence, bioaccumulation and aquatic toxicity of butylal using the USEPA PBT Profiler indicate low persistence in water, soil and air, low bioaccumulation potential, moderate persistence in sediments, and moderate aquatic toxicity (USEPA PBT 2006). Information from the manufacturer indicates that it causes low to moderate harm to aquatic life with long-lasting effects (GHS Aquatic Chronic 3) (ECHA). However, the solvent manufacturer also states that butylal has low solubility in water, and therefore would not reach a high enough concentration in the aquatic environment to cause harm; this conclusion is also supported by a review of butylal by the New York State Department of Environmental Conservation (NYSDEC 2011).

Questions also still remain regarding breakdown products of butylal. A German study reported that n- butylal breaks down in the atmosphere into alkoxymethyl formates and aldehydes (Barnes 1999).

Health Effects

Based on studies provided by the manufacturer, butylal may cause skin irritation (ECHA), but is not irritating to the eyes and has not been found to be mutagenic (LC 2011); other companies' MSDS's indicate "irritating to the eyes." The neutralizer (Alkanon), used in acetal systems to eliminate fatty or organic acids from solution that could denature the solvent, has been classified by IARC as a Group 3 chemical, which means that there is not sufficient evidence with which to evaluate its carcinogenicity to humans. Butylal has not been reviewed by IARC for carcinogenicity. Studies of acute toxicity on rodents indicate an oral LD_{50} of 6,873 mg/kg, and dermal LD_{50} of greater than 2,000 mg/kg (LC 2011). There are currently no data available on central nervous system or other target organ effects, reproductive toxicity, or other chronic health effects.

Safety Concerns

Because butylal is a combustible liquid (flash point of 144°F), precautions must be taken to minimize the risk of fire (see the "Safety Concerns" section under "High Flash Hydrocarbons"). Butylal is a volatile organic compound based on its boiling point of 357°F.

Regulatory

Acetals are not currently regulated at the federal or state level. No permissible or recommended exposure limit has been established for this substance. Fire code requirements will be similar to the high flash hydrocarbon systems.

Propylene Glycol Ethers

Glycol ethers are a class of petroleum solvents that were introduced as an alternative to perc in dry cleaning in the late 1990s.

Technical Information

Chemistries

Glycol ethers for use in dry cleaning have historically included dipropylene glycol tert-butyl ether, CAS# 132739-31-2 (Rynex 3®), a combination of aliphatic dipropylene glycol ether and hydrocarbon (Impress® and Gen-X), or dipropylene glycol n-butyl ether, CAS# 29911-28-2, combined with liquid CO_2 (Solvair®).

Equipment and Process

Glycol ether systems can typically be used with a hydrocarbon machine after minor modifications. Because of the flash point of glycol ethers, the processing equipment is similar to that used for hydrocarbon solvents. Some of the machines are equipped with a refrigerated condenser (for vapor recovery) while others are not. It has been reported that at least one glycol ether system has a cycle time longer than perc (IRTA 2005).

Performance

Glycol ethers are reported to be gentle on fabrics, requiring few pre- or post-spotting treatments (IRTA 2005).

Waste Management

Waste from these systems are not considered hazardous under the RCRA; however, many vendors recommend that it be treated as hazardous nonetheless. The waste from a glycol ether system is likely to be acceptable for discharge to a wastewater treatment system under an approved discharge agreement.

Financial

The cost of glycol ether solutions is between $28 and $30 per gallon (Caled Industries 2012). The cost of a propylene glycol ether machine was $56,000 in 2004 in California (IRTA 2005). Based on one case study shop in California, the total cost per pound cleaned was estimated at $1.14 (IRTA 2005).

Environmental, Health and Safety

Environmental Impacts

Glycol ether-based garment care solvents are volatile and biodegradable with flash points ranging from 160°F for the Impress® blend, to 212°F for the Solvair® solvent. The boiling point of propylene glycol ethers ranges from 368°F to 446°F, and they are VOC's (OEHHA 2010). These substances are predicted to have low persistence in water, soil and air, while having moderate persistence in sediment (USEPA PBT 2006). Both bioaccumulation and aquatic toxicity are estimated to be low (USEPA PBT 2006).

Health Effects

Propylene glycol ethers are dermal, ocular and respiratory irritants (IUCLID 2000, CARB 2010, ILO 1998). Acute exposure to high levels in humans may result in CNS effects and liver and/or kidney damage (ILO 1998). Neither IARC nor EPA has classified propylene glycol ethers for carcinogenicity. Oral rat LD_{50} values range from 3,700 to

4,400 mg/kg (SIDS 2003, TR 95 2005). Emerging research has found that the β isomer of the propylene glycol ether (which represents approximately 1% of the substance composition) metabolizes in a similar manner to the ethylene glycol ethers, which suggests a potential reproductive toxicity effect similar to what is exhibited by the ethylene glycol ethers (INSERM 2006). Given the low concentration of the β isomer in commercially available propylene glycol ethers and the uncertainty of adverse effects, reproductive toxicity is of low concern at this time. However, further research is warranted.

Safety Concerns

The common propylene glycol ethers are classified as Class IIIA or IIIB combustible liquids. (See the "Safety Concerns" section under "High Flash Hydrocarbons.")

Regulatory

Glycol ethers are combustible liquids, and so facilities must comply with all fire safety codes (see the "Regulatory" section under "High Flash Hydrocarbons"). There are no specific waste management restrictions. There are no specific MA DEP air requirements associated with propylene glycol ethers. However, if emissions exceed the potential to emit over 1 ton per year, the owner must submit a plan application under 310 CMR 7.02. This is unlikely to occur in dry cleaning facilities. Occupational exposure limits have not been established.

Siloxane

The current volatile methyl siloxane used in dry cleaning is the cyclic VMS decamethylcyclopentasiloxane (D5). D5 is the solvent used in the GreenEarth® dry cleaning system.

Technical Information

Chemistries

Volatile methyl siloxane cleaners consist of a modified liquid silicone that is a combustible liquid. The CAS # for cyclic VMS decamethylcyclopentasiloxane (D5) is 541-02-6.

Equipment and Processes

Siloxane-based chemistries may be used in multi-solvent machines, and GreenEarth® Cleaning claims that most 4th and 5th generation machines currently being used with hydrocarbons can be modified for use with D5. Because siloxanes are combustible, the equipment needs to be specially designed to meet fire safety codes. The GreenEarth® process requires a longer cycle time than perc or hydrocarbons; the average cycle time is 53 to 58 minutes (DLI 2007). Since D5 has a specific gravity that is similar to water, it is necessary to separate the solvent from water prior to disposal.

Performance

D5 is a less aggressive cleaner than perc, and therefore can clean delicates (such as silks, wedding gowns, drapes, suedes, leathers and beaded garments) although more pre-spotting treatment may be required. "According to cleaners the D5 gives a very good hand which refers to the feel of the garment; the hand is reportedly even better than hydrocarbon and it makes finishing garments much easier" (Morris and Wolf, 2005).

Waste Management

The manufacturer recommends that a licensed hazardous waste hauler handle the solid waste associated with the use of D5. However, it is not considered to be a hazardous waste (DLI 2007).

Financial

The unit price for the D5 chemistry ranges from $22 to $28 per gallon (Maxwell 2010).

GreenEarth® estimates that start up costs for a new system can range from $30,000 to $55,000 for a machine. GreenEarth® also claims that its product can be used in the same machines that run hydrocarbons. However, with addition of retrofitting costs, the likely total for a new siloxane system that uses a 4th generation or higher perc or hydrocarbon system could be as high as $70,000 (Maxwell 2010).

Based on two case study shops in California, the total cost per pound cleaned ranged from $1.08 to $2.33, averaging $1.71 (IRTA 2005). Operating costs include resource use, which have been estimated to be 54.2 kWh/100 lbs for electricity use and 13.4 therms /100 lbs for natural gas use (Sinsheimer 2009). GreenEarth Cleaning LLC also charges an annual $2,500 affiliation fee for the first machine and $1,250 for additional machines at the same location.

Environmental, Health and Safety

Environmental Impacts

Because GreenEarth® has been identified as a preferred "environmentally friendly" alternative to perc by many dry cleaners in recent years government agencies like California's Office of Environmental Health Hazard Assessment (OEHHA) have made an effort to review available information on D5. Based on its review of relevant data, the California Air Resources Board (CARB) concluded that "available exposure information indicates that the use of D5 as an alternative dry cleaning solvent will not pose a risk to the public living near businesses using D5" (CARB 2008). In a 2008 memorandum from the Chairman of CARB, it is noted that OEHHA conducted an analysis of available information on D5 and identified its "apparent persistence in the environment and in animal and human tissues." Specifically, it is estimated to be highly persistent in sediment and air, while only moderately persistent in soil (USEPA PBT 2006). It is estimated to be moderately bioaccumulative and have high aquatic toxicity (USEPA PBT 2006).

Health Effects

Based on testing results obtained from Dow Corning Corporation, exposure to the high vapor concentrations of D5 can cause uterine tumors in rats (DCC 2005). In addition, developmental and reproductive toxicities have been indicated by various studies (OEHHA 2010). There is some evidence of liver, immune and central nervous system effects (OEHHA 2010). It has low acute toxicity, with an oral LD_{50} value in rats of above 4,800 mg/kg (EC 2007). D5 is indicated as a dermal and ocular irritant (Siltech 2010).

Safety Concerns

The D5 cyclic siloxane is a Class IIIA combustible liquid with a flash point of 170°F (see the "Safety Concerns" section under "High Flash Hydrocarbons"). D5 is a volatile organic compound, but is exempt from Clean Air Act outdoor regulations due to negligible photochemical reactivity (USEPA 1994).

Regulatory

D5 is not regulated under RCRA or CERCLA. While there is no regulatory permissible exposure limit, a Dow Corning MSDS for D5 recommends limiting exposure to 10 ppm (DCC 2011). While the flash point is higher than high flash hydrocarbons, D5 is still a Class IIIA combustible liquid; fire code requirements will be similar to the high flash hydrocarbon systems.

n-Propyl Bromide

N-Propyl bromide (nPB or 1-bromopropane) is considered a "drop-in" replacement for perc in dry cleaning applications, which indicates that it can be used in existing (3rd generation or higher) perc dry cleaning equipment. nPB could be used in hydrocarbon equipment as well, although this would require more extensive modifications (FC 2009). It is similar to perc and other halogenated hydrocarbon solvents, but because it is newer to the market, it is less regulated and there is less information available about its health and environmental effects.

Technical Information

Chemistries

DrySolv® is a patented solvent, developed by EnviroTech International, consisting of 95% nPB (CAS # 106-94-5) and a 5% blend of nitromethane and 1, 2 butyleneoxide, which are used as stabilizers. The manufacturer of DrySolv® also provides a cationic soap (DrySolv® "D") that they recommend for this process to stabilize the solution. Fabrisolv™ XL is another product for dry cleaning applications based on stabilized nPB.

Equipment and Process

As mentioned previously, nPB can be used in existing (3rd generation or higher) perc equipment. However, nPB is known to damage rubber gaskets and seals, causing them to lose their elasticity and fit. It can also degrade cast aluminum, which is sometimes used on equipment doors and other components. In addition, nPB is not compatible with polyurethane and silicone (FC 2009). To avoid leaks and the need for frequent servicing, these components must therefore be replaced with materials compatible with nPB. The cost to replace machine doors to increase compatibility has been estimated to range from $500 to $800. The cost to replace gaskets and seals has been estimated to range from $200 to $400 (Raccon 2010).

Performance

As this solvent use in dry cleaning is relatively new, no performance data was available to include in this report. However, it is anticipated that performance would be similar to that of perc due to the similar nature of the two solvents.

Waste Management

If nPB is used as a drop-in replacement for perc, dry cleaners must consider the likelihood that perc will remain in the system. Perc is likely to remain in gaskets, seals, dead spaces, low spots, and lint within the machine after the conversion to nPB. One reference suggests that it takes up to 6 months of use for residual perc to be reduced to below detectable levels (FC 2009). DrySolv® literature suggests that, because of its higher volatility, there is 25% less waste associated with the solvent distillation process as compared to perc.

Financial

A new machine purchased specifically for nPB use can cost between $40,000 and $60,000, depending on the size (35-55 lbs) of the machine.(Raccon 2010). Conversion from perc to nPB for existing equipment can take a full day and has been estimated to cost from $1,500 to $5,000 (Raccon 2010). The cost of the chemical itself ranges from $40/gal (Raccon 2010) to $64/gal (NEFA 2011).

Environmental, Health and Safety

When used in a system that has been modified to prevent leaks, nPB may be suitable for use in 4th generation or higher perc dry cleaning machines. However, nPB's inherent properties raise concerns with regard to worker exposure.

Environmental Impacts

Under the USEPA Clean Air Act, nPB is a VOC (USEPA 2009). Although it is not currently classified as a hazardous air pollutant or hazardous waste (Sheppard 2008), EPA has been requested to review its status as a hazardous air pollutant. This solvent is persistent in both sediment and air, and is toxic in aquatic environments (USEPA PBT 2006). It is not expected to be persistent in water or soil, and is not expected to bioaccumulate (USEPA PBT 2006). EPA classifies nPB as an Ozone Depleting Substance, although its ozone depleting potential is relatively low (0.013 – 0.018) (EPA 2007).

Health Effects

nPB is considered to be a neurotoxicant and reproductive toxicant (CARB 2008) and is listed on the California Prop 65 List as a developmental toxicant (CAP65 2011). Results from a two-year rat and mouse cancer study show clear evidence of carcinogenic activity (NTP 2011). In human occupational studies, peripheral central nervous system effects, some severe, have been shown. There is also evidence that nPB may have an impact on menstrual cycles, and possible DNA damage at exposures over 100 ppm. Workers exposed to nPB at levels exceeding 90 ppm suffered severe neurological symptoms such as pain in legs, numbness, and difficulty walking (Beck and Caravati, 2003). These symptoms often persisted for months to years. Effects on the reproductive system include low sperm mobility, low male gland weights, and ovarian cycling (Sheppard 2008). Several case reports regarding central nervous system toxicity show severe effects, through both dermal exposure and inhalation (Sheppard 2008). nPB causes eye, nose and throat irritation at concentrations greater than 30 ppm (HESIS 2003). The oral LD_{50} value in rats is above 2,000 mg/kg (ACGIH 2005). Other target organs include liver, kidney, digestive and blood systems (ALBA 2004).

Safety Concerns

This solvent is more volatile than perc, which indicates that releases could pose additional safety risks in the work environment (CARB 2008). It should be noted that nPB exhibits a flash point under some test methods, and not under others, due to the inherent difficulty in determining flash points for halogenated hydrocarbons (ECBI 2002). After expert consideration and court challenge, the European Union classifies nPB as R11, or highly flammable (EU 2009), and some MSDS's may list nPB as highly flammable. Under the Massachusetts fire code, nPB would not be considered to have a flash point. From a practical standpoint, under ordinary operating conditions it is not likely to be a flammability concern (USEPA 2007), but should be used with caution.

Regulatory

For conformance with Massachusetts fire regulations, the flash point of nPB, which has a viscosity of 0.3 to 0.5 centiStokes, is determined in accordance with ASTM D 56, Tag Closed Cup (NFPA 30). Tests using this method have shown no flash point for nPB; therefore, in Massachusetts nPB is not considered flammable.

nPB received Significant New Alternatives Policy (SNAP) approval from EPA as an alternative to known ozone-depleting chemicals used in metals, electronics and precision cleaning, limited to equipment formulated to clean below the boiling point, but was not approved for use as an aerosol or carrier solvent in adhesives, and only approved in coating applications that have data demonstrating an ability to maintain acceptable exposure levels (USEPA 2007)[2]. While this currently has no direct regulatory effect on the dry cleaning industry, it is important to note that the use of nPB is being monitored and regulated by EPA. While OSHA does not have a permissible exposure limit established for nPB, in 2005 the American Conference of Governmental Industrial Hygienists (ACGIH) established a recommended threshold limit value (TLV) of 10 ppm for an eight-hour time-weighted average workday for exposure (ACGIH 2006). ACGIH has also released a Notice of Intended Change for nPB which recommends lowering the TLV to 0.1 ppm (ACGIH 2012).

In addition, nPB is now a listed toxic chemical under the Toxics Use Reduction Program in Massachusetts, which means that users of nPB are required to report and plan on reducing the use of nPB if they exceed certain thresholds (TURA 2011).

Due to the potential for residual perc to remain in equipment, cleaners should ensure that waste generated in a retrofitted nPB system is not contaminated with sufficient perc to render it a characteristic hazardous waste.

[2] The SNAP Program is EPA's program to evaluate and regulate substitutes for the ozone-depleting chemicals that are being phased out under the stratospheric ozone protection provisions of the Clean Air Act (CAA).

IV. Comparison of Alternatives to Perchloroethylene in Professional Garment Cleaning

This section compares perchloroethylene and seven alternatives on four categories of criteria:

- Technical performance
- Financial factors
- Environmental and human health impacts
- Regulatory and safety considerations

Tables listing the alternatives and assessment criteria are provided to facilitate comparisons. This information is also summarized in Section I of this report.

Technical Performance Comparison of Alternatives

Key technical parameters for dry cleaners include cycle time, load capacity, and quality of cleaning. Additional considerations include pre-spotting and maintenance requirements, additional finishing or control equipment, equipment availability and vendor support, solvent odor issues, and waste management. Table 4 provides a summary of several technical performance assessment criteria important to dry cleaners.

Observations about the technical performance of the alternatives as summarized in Table 5 include:

- Wet cleaning cycle times are typically shorter than other systems – using a separate washer and dryer allows the two cycles to overlap, thereby saving time. Massachusetts cleaners that have converted to dedicated wet cleaning claim that they have significantly reduced their time at the spotting board. This is at least in part because most of the stains on clothes are well suited to removal by the water and detergent chemistries and technology. Wet cleaning exhibits better cleaning results for most fabric types, including the fact that clothes are less dingy than when cleaned with a recycled solvent. Massachusetts cleaners have stated that "whites are whiter and brights are brighter."
- Hydrocarbon systems exhibit similar productivity to that of perc-based systems, and are said to produce a cleaner garment overall than some of the other solvent-based systems.
- CO_2 systems exhibit better productivity than perc-based systems, but may require more spotting for sufficient cleaning.
- According to the manufacturer, the acetal system has a similar cycle time to perc, a wide range of load capacities and is able to clean a wide range of fabrics with minimal pretreatment.
- Performance of nPB is expected to be similar to that of perc-based systems. It is reported that nPB systems would have similar difficulty with certain fabrics, and excessive color "bleed," as perc-based systems.
- Longer cycle times and smaller load capacities in propylene glycol ether and siloxane-based systems make them less productive than perc-based systems.
- The spotting requirements for propylene glycol ether systems are reported to be less demanding than for perc. Propylene glycol ether systems are compatible with a wider range of fabrics and garments than perc-based systems.

- Siloxane systems are reported to require more pre-spotting than perc systems.

Table 4: Dry Cleaning Alternatives - Technical Data

Assessment Criteria	Perc	Wet Cleaning	Carbon Dioxide	High Flash Hydrocarbon	Acetal	Propylene Glycol Ethers	Siloxane	n-Propyl Bromide
Cycle time (min)	45	20-40	35-45	60-75	60-65	> 45	53-58	45
Load capacity (lbs)	50	20-75	60	35-90	40-90	43	55	50
Cleaning capability	Aggressive[3]	Less aggressive	Less aggressive	Less aggressive	Unclassified	Unclassified, but gentle on fabrics	Less aggressive	Aggressive
Fiber/garment types that are difficult for this alternative	Leather, suede, beads, delicates	Leather, suede and fur	Triacetates, specially dyed acetates	Vinyl appliqués	Appliqués or decorations glued to fabric	None identified	None identified	Leather, suedes, beads, delicates
Time required for pre-spotting	Medium	Low	High	Medium	Low	Low	High	Low
Equipment compatibility	Perc equipment	Wet cleaning equipment	CO_2 equipment	Hydrocarbon	Retrofit hydrocarbon or new acetal system	Retrofit 4th Gen or higher hydrocarbon	Retrofit perc or hydrocarbon 4th Gen or higher	Retrofit perc or hydrocarbon 4th Gen or higher
Special equipment	Vapor recovery equipment	Additional finishing equipment and training required	High pressure equipment	Combustible – must meet fire safety codes	Combustible – must meet fire safety codes	Combustible – must meet fire safety codes	Combustible – must meet fire safety codes	New seals, gaskets and doors may be required
Waste management concerns	Handle spent solvent and solids as hazardous waste	Requires discharge to sewer or holding tank	Waste soils and lint do not require special handling	Considered as waste oil in MA, to be disposed of as hazardous waste; empty containers may contain residual solvent and may be dangerous	Waste solvent disposed of as industrial waste	Difficult to distill water prior to waste mgmt	Separate solvent from water before disposal; not required to be treated as hazardous waste	If used as a drop in replacement, residual perc may be present for up to 6 months

[3] The term "aggressive" refers to the ability of the solvent/system to thoroughly remove soils from any garment. This also encompasses the potential for causing wear on garment fibers.

Financial Comparison of Alternatives

Dry cleaners are typically small operations where capital equipment costs can dictate decision-making. Table 5 provides a summary of costs associated with the seven alternatives as compared with perc.

Based on the available financial data presented in Table 4, the following highlights are apparent:

- Wet cleaning requires the least amount of energy of the other systems, both in electricity and in natural gas usage. Studies conducted by the Massachusetts Toxics Use Reduction Institute (Onasch 2010) indicate that significant energy reductions can be associated with the use of wet cleaning over perc-based dry cleaning systems, when it is the sole system used at a facility, eliminating the use of solvent recovery systems.
- Butylal shows promise of energy use reduction as it reportedly has a much lower energy requirement for solvent distillation, requiring only half the BTUs of a perc system.
- Wet cleaning has comparable equipment and operational costs to perc, although detergent costs are higher than perc, and more detergent is required for the process.
- The capital costs for the acetal system are somewhat higher than perc, but facilities may see payback on their investment through lower steam heat costs. As this chemistry is new to the market, it is expected that additional studies will reveal how the costs play out for facilities using the acetal chemistry.
- Costs for nPB are significantly higher than for perc based on the cost per gallon of the chemistries. In addition, as noted in the regulatory section of this report, nPB use may result in additional Massachusetts regulatory requirements if facilities exceed TURA reporting and planning thresholds.
- The carbon dioxide option is cost-prohibitive for many small shops due to the high upfront capital cost of equipment. However, if installed, the chemical costs may be lower for a facility.
- In addition to the information presented in Table 4, cleaners may find it helpful to know that existing higher generation (4^{th} generation and higher) perc or hydrocarbon systems could be retrofitted for use with nPB, siloxane or acetal.

Table 5: Dry Cleaning Alternatives – Financial Data

Assessment Criteria	Perc	Wet Cleaning	Carbon Dioxide	High Flash Hydro-carbons	Acetal	Propylene Glycol Ethers	Siloxane	n-Propyl Bromide
Equipment costs (ranges relate to capacity, quality and features of machines)	$40,000 to $65,000	$36,000 to $61,000	$100,000 to >$150,000	$38,000 to $75,000	$50,000 to $100,000	$56,000	$30,500 to $55,000	$40,000 to $60,000 (or retrofit costs for existing perc equipment)
Solvent costs (per gallon)	$17	$.007/gal (water use fee) + $25-$31/gal (detergent)	$0.18/lb CO_2 + $40/gal detergent	$14-$17	$28-$34	$25-$30	$22-$28	$40-$64
Total cost per pound cleaned (range and average)[4]	$0.63 - $1.94 Avg: $1.02	$0.57 - $1.32 Avg: $1.10	$1.40	$0.73 - $1.02 Avg: $0.88	Unavailable	$1.14	$1.08 - $2.33 Avg: $1.71	Unavailable
Estimated electricity usage for equipment operation (kWh/100 lbs)	26.6	9.3	30.9	35.5	Assumed to be similar to hydrocarbon	Unavailable	54.2	Unavailable
Estimated natural gas usage for hot water and steam heat for drying, distillation, and pressing (therms/100 lbs)[5]	12	9	7.3-14.2	13.1	Natural gas use for solvent distillation more energy efficient than HC or perc	Unavailable	13.4	Unavailable

[4] The cost per pound cleaned, based on case study facilities in California, includes capital, solvent, licensing, detergent, electricity, gas, spotting labor, finishing and maintenance labor, maintenance of equipment, compliance, and hazardous waste disposal costs (IRTA 2005). For technologies with multiple case study facilities, both the range and average cost are shown.

[5] Sinsheimer 2009

Environmental and Human Health Comparison of Alternatives[6]

A primary concern for dry cleaners is worker and customer exposure to volatile organic emissions. In addition, the historical experience of soil and groundwater contamination related to dry cleaning operations, and the financial liability associated with remediation of these events, further underscores the importance of selecting safer alternatives. Table 6 provides a summary of environmental and human health data associated with the alternatives.

It is important to note that the environmental and human health data associated with the wet cleaning system is based on the detergent and additive package that is largely responsible for the cleaning performance (as opposed to the solvent, which for this technology is water). Similar detergents and performance booster formulations are added to other solvent systems, including perc, but typically at lower concentrations. In wet cleaning, the detergent/additive package typically constitutes 3% to 5% by volume of the overall solution in which clothes are placed. In contrast, the detergent/additives that are used in other systems make up no more than 1% by volume of the overall solution in which clothes are placed.

The following are highlights of the environmental and human health considerations of alternative solvents in comparison to those of perc:

- The environmental and human health data analyzed for the wet cleaning system demonstrates that it poses the least potential risk to human health and the environment of the alternatives assessed.
- The CO_2 system generally exhibits better environmental and human health characteristics than perc systems. CO_2 systems have unique concerns associated with high pressure equipment and the potential for leaks and associated exposure to high concentrations of CO_2.
- Modeled information for butylal (the acetal) indicates similar aquatic toxicity characteristics as those for perc. Butylal is a volatile organic compound, indicating a potential for occupational exposure. Because the acetal solvent Solvon K4 is a new product, very little test data is currently available. The majority of human health effect data referenced here is based on product data provided by the manufacturer. The gaps in data may lead to a different comparative conclusion relative to perc after more is learned about the environmental and human health implications of acetals.
- Propylene glycol ethers are not expected to be harmful to the environment with regard to persistence, bioaccumulation or aquatic toxicity. Health effects of concern pertain to irritation and potential effects on the liver, kidneys or CNS. In addition, studies suggest that metabolism of one minor element of the overall composition might be linked with reproductive toxicity concerns.
- High flash point hydrocarbons present a high concern for aquatic toxicity, should there be a release into the aqueous environment. There are also concerns around bioaccumulation and effects on the central nervous system.
- D5 exhibits persistence, bioaccumulation potential, and aquatic toxicity characteristics that are of concern. In particular, modeling data indicates that D5 is highly persistent in sediments and air, and has

[6] Citations for studies that form the basis for the summary statements in this section are provided in Section III of this document.

high aquatic toxicity. Studies indicate that D5 may represent a reproductive hazard, and one recent animal study shows evidence of carcinogenicity.

- While nPB, a volatile organic compound, is less persistent in most media than is perc, it is highly persistent in air and, because of its volatility, represents a potentially significant occupational exposure risk. nPB is also highly toxic to aquatic species. nPB has been determined to be a reproductive and developmental toxicant and exhibits central nervous system effects. Finally, recent studies by the National Toxicology Program indicate clear evidence of carcinogenicity in certain animals.

Table 6A: Dry Cleaning Alternatives – Ecological and Environmental Information

Assessment Criteria	Perc	Wet Cleaning[7]	Carbon Dioxide	High Flash Hydrocarbons	Acetal	Propylene Glycol Ethers	Siloxane	n-Propyl Bromide
Representative CAS #(s)	127-18-4	106232-83-1, 26027-37-2, 69227-21-0, 112-34-5, 29923-31-7, & 61791-32-0[8]	124-38-9	68551-17-7, 64742-48-9	2568-90-3	29911-28-2, 132739-31-2	541-02-6	106-94-5
Persistence (water, soil, sediment and/or air)[9]	M (water), H (soil, sed, air)	L (water, soil, air), M (sed)	NA	L (water, soil, air), M (sed)	L (water, soil, air), M (sed)	L (water, soil, air), M (sed)	L (water), M (soil), H (sed, air)	L (water, soil), M (sed), H (air)
Bioaccumulation[10]	Low	Low	NA	Mod	Low	Low	Mod	Low
Aquatic toxicity (mg/L)[11]	Mod (5)	Low to Mod[12]	Low (35)	High (0.023)	Mod (2.9)[13]	Low (84)	High (0.021)	High (0.051)
Volatile Organic Compound	Yes, Exempt[14]	No[15]	No	Yes	Yes	Yes	Yes, Exempt[16]	Yes

[7] Important note: The primary solvent in wet cleaning is water. For the purposes of this table, the EH&S information provided applies to undiluted detergents and other additives common in wet cleaning processes, which are also common in other cleaning systems. These additives are present in amounts of 3% to 5% in wet cleaning, and are used in lesser amounts in other systems (typically around 1%).

[8] These represent the primary (i.e., present in additive formulations at or greater than 1% by volume) undiluted detergents and additives included in this assessment.

[9] Persistence criteria in each of the environmental compartments: Air [L<=2 days, H>2 days]; Sediment, Soil & Water [L<60 days, M>=60 days, H>180 days]. Low (L) is considered to be 'Not Persistent.'

[10] Bioaccumulation criteria: Low (Not Bioaccumulative) <1,000, Mod (Bioaccumulative) >= 1,000.

[11] Fish ChV (mg/l) Toxicity criteria: Low (Not Toxic) > 10mg/l or no effects at saturation, Mod (Toxic) <10 mg/l, High (Toxic) <0.1 mg/l.

[12] This system is characterized as Low aquatic toxicity, with the exception of one constituent of the detergent package Lanadol Aktiv; it contains 1-5% of Oleic acid Monoethanolamid, ethoxylated (CAS# 26027-37-2), which is predicted to be moderately toxic but readily biodegradable.

[13] This value (based on the PBT Profiler model) differs from the Kreussler MSDS which states Solvon K4 is insoluble in water, and would therefore not reach a concentration in water sufficient to cause aquatic toxicity.

[14] Exempt from USEPA and MassDEP VOC regulations by rule, due to determination of negligible photochemical reactivity.

[15] This assessment is for the overall system composition. One component of the cleaning package Lanadol Avant contains 1-5% of 2-(2-butoxyethoxy) ethanol (CAS# 112-34-5), which is a VOC based on its boiling point of 439°F.

[16] Exempt from USEPA and MassDEP VOC regulations due to determination of negligible photochemical reactivity; U.S. EPA, 1994, direct final rulemaking: D5 specifically exempt from regulation as a Volatile Organic Compound (VOC).

Table 6B: Dry Cleaning Alternatives – Health Effects

Assessment Criteria	Perc	Wet Cleaning[17]	Carbon Dioxide	High Flash Hydrocarbons	Acetal[18]	Propylene Glycol Ethers	Siloxane	n-Propyl Bromide
Carcinogenicity	Probable Human Carcinogen (IARC 2A)	Not classified by IARC	Not classified by IARC	Not classified by IARC	Not classified by IARC	Not classified by IARC	Some evidence	Clear evidence in animal studies by NTP
Reproductive or developmental toxicity	Yes	Negligible[19]	No data available	No data available	No data available	No[20]	Studies indicate concern	Yes
LD_{50}	Oral, rat, 2,629 mg/kg	NA[21]	NA	Oral, rat, >5,000 mg/kg	Oral, rat, 6,873 mg/kg	Oral, rat, >3700 mg/kg	Oral, rat, >4,800 mg/kg	Oral, rat, >2,000 mg/kg
Dermal/ocular/ respiratory irritant	All	Dermal, ocular	Dermal, ocular	All	Possibly dermal, ocular	All	Dermal, ocular	All
Central nervous system effects	Yes	Negligible[22]	No[23]	Yes	No data available	Yes	Some evidence	Yes
Other target organs	Liver, kidneys, immune and hematologic system	Negligible[24]	Heart, lungs	Lungs, kidneys	None known	Liver, kidneys	Liver, immune system	Liver, kidney, digestive & blood systems
Recommended exposure limit	25 ppm[25]	NE	5000 ppm[26]	100 ppm[27]	NE	NE	10 ppm[28]	10 ppm[29]

NA = not applicable; NE = not established

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[17] Important note: The primary solvent in wet cleaning is water. For the purposes of this table, the EH&S information provided applies to undiluted detergents and other additives common in wet cleaning processes, which are also common in other cleaning systems. These additives are present in amounts of 3% to 5% in wet cleaning, and are used in lesser amounts in other systems (typically around 1%).

[18] Except where noted, information on acetals is provided by the manufacturer, and has not been independently assessed.

[19] Lanadol Avant contains 1-5% of 2-(2-butoxyethoxy) ethanol (CAS# 112-34-5), which can cause fertility impairment or teratogenesis (HAZMAP 2011). Concentration in washer is approximately 0.1%, which is below accepted de minimis.

[20] Possible reproductive effects from minor β-isomer of propylene glycol ethers, which comprises ~1% of the substance and metabolizes to alkoxyacid. New studies confirmed the minor β-isomer developmental toxicity and showed, for the first time, testicular toxicity. (INSERM 2006).

[21] The oral, rat LD_{50} value for one constituent of Lanadol Avant, Alcohols C13-C15 branched and linear, ethoxylated (CAS #106232-83-1) [present at up to 35% of the individual detergent formulation], is >2,000 mg/kg. This value pertains to the individual chemical and may not be relevant with regard to the mixture.

[22] See note 19 - 2-(2-butoxyethoxy) ethanol (CAS# 112-34-5) includes the central nervous system as a target organ.

[23] At high concentrations (>6% in air), CO_2 causes CNS effects, at sufficient concentrations causes asphyxiation.

[24] See note 19 - 2-(2-butoxyethoxy) ethanol (CAS# 112-34-5) includes kidneys, liver, the heart and blood as target organs.

[25] ACGIH TWA-TLV (ACGIH 2006)

[26] OSHA PEL (NIOSH 2004)

[27] ACGIH TWA-TLV for Stoddard Solvent; No values established for specific hydrocarbons in these products. (ACGIH 2006)

[28] Manufacturer's recommended limit (DCC 2011)

[29] ACGIH TWA-TLV (ACGIH 2006)

Regulatory and Safety Comparison of Alternatives

Many of the alternatives to perc have safety considerations, in particular, flammability. These characteristics often require a regulatory framework to ensure safe operation. These requirements may be a significant factor for small dry cleaning businesses. The Massachusetts Board of Fire Prevention Regulations (527 CMR 3) adopts NFPA 32 (National Fire Protection Association code for dry cleaning plants) by reference. In addition, dry cleaners using combustible solvents should check with their local fire department to determine applicability of Massachusetts process safety management regulations 527 CMR 33 (MADFS).

Table 7: Dry Cleaning Alternatives – Regulatory and Safety Information

Regulatory Considerations	Perc	Wet Cleaning	Carbon Dioxide	High Flash Point Hydrocarbons	Acetal	Propylene Glycol Ethers	Siloxane	nPropyl Bromide
Regulatory Information								
Regulated as hazardous air pollutant (HAP) under the Clean Air Act	Yes - HAP	No	No	No	No	No	No	No
Regulated as VOC under the Clean Air Act (CAA) NAAQS	No, exempt under CAA NAAQS	No	No	Yes	Yes	Yes	No, exempt under CAA NAAQS	Yes
Solid waste regulated as hazardous (US RCRA or MassDEP)	Yes - Listed hazardous waste	No	No	Waste oil must be managed as a hazardous waste in MA	No	No	No	No
Flammability classification (solvent class) (NFPA 32)	None	None	None	Combustible liquid (Class IIIA solvent)	Combustible liquid (Class IIIA solvent)	Combustible liquid (Class IIIA or IIIB solvent)	Combustible liquid (Class IIIA solvent)	NA[29]
Chemical reportable under US EPA Toxics Release Inventory	Yes	No	No	No	No	No	No	No
Chemical reportable under Massachusetts Toxics Use Reduction Act	Yes, higher hazard substance	No	No	No	No	No	No	Yes

Regulatory Considerations	Perc	Wet Cleaning	Carbon Dioxide	High Flash Point Hydrocarbons	Acetal	Propylene Glycol Ethers	Siloxane	nPropyl Bromide
Regulatory Information (continued)								
System regulated under Massachusetts Environmental Results Program	Yes	No	No	No	No	No	No	No
Other regulatory considerations	Leak detection and repair required	Wastewater may require permit for discharge to sewer. MA facilities on septic must discharge to holding tank or obtain groundwater discharge permit.	High pressure storage may require compliance with codes	Compliance with local fire safety codes required	Compliance with local fire safety codes required	Compliance with local fire safety codes required	Compliance with local fire safety codes may be required	None
Physical Safety Information								
Flash point (°F)	NA[30]	NA	NA	160 - 212	142	NA or 72[29]	171	NA
Other safety concerns	Combustion byproducts include HCl and phosgene	None	Safety hazard associated with high pressure equipment	None	None		None	Combustion byproducts include HBr

NA = not applicable

[30] Note: there are inherent difficulties with determining flash point of halogenated hydrocarbon liquids. Some test methods show no flash point for nPB; others show a flash point of 72°F (ECBI 2002). In MA nPB is considered non-flammable; in the European Union it is classified as R11 (highly flammable) (EU 2009).

The following highlights are indicated from the safety and regulatory data presented in Table 7:

- Wet cleaning wastewater discharges to sewer/publicly owned treatment works may require a municipal discharge permit agreement; cleaners must contact their municipal operator to determine what restrictions may apply. Common restrictions include limits on the amount of oils and grease or suspended solids, as well as pH limitations on wastewater discharges. Wet cleaning wastewater may not be discharged to septic systems without first obtaining a groundwater discharge permit in Massachusetts – a costly and time-intensive process. Utilizing an industrial wastewater holding tank that complies with the applicable regulations, prior to transporting wastewater to a publicly owned treatment works, is also an option for cleaners on septic systems. No other regulatory or safety considerations apply to wet cleaning systems.
- Cleaners should be aware of the hazard and regulatory requirements of spotting chemicals, regardless of which alternative system they are using.
- Compliance with local fire safety codes is likely required with siloxane, propylene glycol ether systems, and acetals, which are volatile and combustible. No other regulatory compliance requirements have been identified. Because the acetal solvent is a new technology for dry cleaning it is unclear whether regulatory restrictions may be developed as more information becomes available.
- The high pressure CO_2 vessels may be subject to local building code restrictions for high pressure equipment. Physical safety concerns are associated with risk of explosion and the ability of high concentrations of released CO_2 to asphyxiate workers in the event of a leak.
- Compliance with local fire safety codes is required for all operations using hydrocarbons. In addition, the solid waste associated with a hydrocarbon system is considered waste oil which, in Massachusetts, must be managed as hazardous. HC systems have inherent safety concerns associated with the combustibility of the primary solvent.
- nPB is now reportable to MassDEP under TURA as a listed toxic chemical. Because it is a VOC, there are air regulations that apply to nPB systems.

Summary

The alternatives assessed in this report represent technically and economically feasible alternatives to perc dry cleaning systems. The ability of individual facilities to justify the financial impact of switching to one of the alternatives varies. From a performance perspective, the client base (and its associated cleaning needs) and the skill of the facility employees are important factors to consider when evaluating which alternative satisfies individual facility needs. From a regulatory perspective, the alternatives assessed may require some additional attention, but in general, do not have restrictions that negate the feasibility of the alternative.

The primary differences between the various alternatives are associated with the environmental and human health and safety characteristics of the alternative systems. Perc is a probable human carcinogen with acute toxicity characteristics, negative impacts on the central nervous system and worker exposure concerns associated with its volatile nature. Overall the alternative solvents assessed in this report exhibit less persistence, potential to bioaccumulate, or aquatic toxicity in the environment than perc. With the exception of nPB, the alternatives exhibit overall human health characteristics that are preferable to perc. nPB does not appear to be a safer alternative to perchloroethylene, as there is evidence of carcinogenicity, reproductive toxicity and neurotoxicity. Toxicological data are lacking for some of the alternatives – particularly the new acetal-based system – making the human health assessment incomplete. Because of these data gaps, it is possible that future analyses will identify additional impacts associated with the use of this or other systems.

A major concern that exists for many of the alternatives is flammability. Wet cleaning and carbon dioxide have no flammability concerns. The other alternatives were rated as combustible, thus requiring specialized equipment to protect against fire or explosion.

For waste disposal, facilities need to be aware of MassDEP regulations that require industrial wastewater, including that from professional wet cleaning or laundering processes, to be discharged to a public sewer or an appropriate holding tank for off-site transfer. In some instances, it is also possible to obtain a groundwater discharge permit for a septic system, although obtaining such a permit is a costly and time-intensive process.

The following table summarizes the comparison of the seven alternatives and perc, based on technical, economic, environmental, regulatory and human health criteria. Color coding has been used which indicates preferability of alternatives purely from an EH&S perspective. The key environmental and human health criteria shown on this table are considered the most relevant for dry cleaning applications, though other criteria were assessed and are included in Section III of this report.

Dry cleaners seeking safer alternatives to perc should consider the key environmental and human health criteria initially, and then apply the financial and technical criteria to their individual facilities to determine the best alternative for their facility.

Summary Table: Comparison of Perc and Seven Garment Cleaning Alternatives

Key Assessment Criteria		Perc (reference)	Wet Cleaning	Carbon Dioxide	High Flash point Hydro-carbons	Acetal	Propylene Glycol Ethers	D5 Siloxane	n-Propyl Bromide
Technical Performance	Cycle time	45 min	20-40	35-45	60-75	60-65	>45	53-58	45
	Load capacity	50 lbs	20-75	60	35-90	40-90	43	55	50
	Materials system may have difficulty with	Leather, suedes, beads, delicates	Leather, suede and fur	Triacetates, specially dyed acetates	Vinyl appliqués	Appliqués or decorations glued to fabric	None identified	None identified	Leather, suedes, beads, delicates
	Spotting requirements	Moderate	Low	High	Moderate	Low	Low	High	Low
Financial	Equipment	$40,000 - $65,000	$36,000 - $61,000	$100,000 - >$150,000	$38,000 - $75,000	$50,000 - $100,000	$56,000	$30,500 - $55,000	$40,000 - $60,000 or retrofit cost
	Chemical cost per gallon	$17	$0.007/gal (water); $25-$31/gal (detergent)	$0.18/lb ($CO_2$); $40/gal (detergent)	$14-$17	$28-$34	$25-$30	$22-$28	$40-$64
	Cost per pound cleaned (range and average)	$0.63 - $1.94 Avg: $1.02	$0.57 - $1.32 Avg: $1.10	$1.40	$0.73 - $1.02 Avg: $0.88	Unavailable	$1.14	$1.08 - $2.33 Avg: $1.71	Unavailable
	Electricity usage (kWh/100 lb)	26.6	9.3	30.9	35.5	Similar to hydrocarbon	Unavailable	54.2	Unavailable

Key Assessment Criteria		Perc (reference)	Wet Cleaning	Carbon Dioxide	High Flash point Hydro-carbons	Acetal	Propylene Glycol Ethers	D5 Siloxane	n-Propyl Bromide
Environmental	Persistence (water, soil, sediment and/or air)	M (water), H (soil, sed, air)	L (water, soil, air), M (sed)	NA	L (water, soil, air), M (sed)	L (water, soil, air), M (sed)	L (water, soil, air), M (sed)	L (water), M (soil), H (sed, air)	L (water, soil), M (sed), H (air)
	Bioaccumulation	Low	Low	NA	Moderate	Low	Low	Moderate	Low
	Aquatic toxicity	Moderate	Low to Moderate	Low	High	Moderate	Low	High	High
Human Health	Recommended exposure limits	25 ppm	NE	5000 ppm	100 ppm	NE	NE	10 ppm	10 ppm
	Central nervous system effects	Yes	No	No	Yes	No data available	Yes	Some Evidence	Yes
	Carcinogenicity	Probable human carcinogen	Not classified by IARC	Not classified by IARC	Not classified by IARC	Not classified by IARC	Not classified by IARC	Some evidence	Clear evidence in animal studies by NTP
	Reproductive/ developmental toxicity	Yes	Negligible	No data available	No data available	No data available	No	Studies indicate concern	Yes
Physical Safety	Flash point/ flammability	NA/Not Flammable	NA/Not Flammable	NA/Not Flammable	140-145°F/ Combustible liquid	144°F / Combustible liquid	160-212°F / Combustible liquid	171°F / Combustible liquid	NA or 72°F (Flammability dependent on test method)

Key Assessment Criteria		Perc (reference)	Wet Cleaning	Carbon Dioxide	High Flash point Hydro-carbons	Acetal	Propylene Glycol Ethers	D5 Siloxane	n-Propyl Bromide
Applicable Regulatory	Clean Air Act Hazardous Air Pollutant (HAP)	Yes, HAP	No	No	No	No	No	No	No
	Clean Air Act NAAQS VOC	No, Exempt	No	No	VOC	VOC	VOC	No, Exempt	VOC
	Massachusetts regulated (TURA, ERP)	TURA Higher Hazard Substance, ERP	No	No	No	No	No	No	TURA
	Hazardous waste disposal required	Yes - Listed hazardous waste	No	No	Yes Waste Oil = Hazardous Waste in MA	No	No	No	No; monitor for residual perc if using retrofitted machine
	Wastewater	No wastewater	Discharge to sewer or holding tank	No wastewater	No wastewater	No wastewater	No wastewater	No wastewater	No wastewater

NA = Not applicable; NE = Not established

Appendix A – Solvent Categories & Chemical Information

Category	Trade name	Solvent		Boiling Point (°F)	Flash Point (°F)
		CAS #	Chemical Name		
Perchloroethylene		127-18-4	perchloroethylene	250	N/A
nPropyl Bromide	Drysolv®, Fabrisolv™ XL	106-94-5	stabilized n propyl bromide	160	72 or N/A
High Flash Hydrocarbons	DF2000™ Fluid	64742-48-9	Naphtha (petroleum), hydrotreated heavy	365-412	142
	EcoSolv® (Chevron Phillips)	68551-17-7	C10-C13 Isoalkanes	372-406	142
	ShellSol D60	64742-88-7	high flash aliphatic mineral spirit	350-417	140
	PureDry, Niran Technology – *may no longer be available, trademark cancelled 2010*		isoparaffinic HC + 3M chemical additive, 95% mineral spirits (C9 - C12 aliphatic HC), contains HFE 7200 (ethylperfluoroisobutyl ether and ethyl perfluorobutyl ether), FC-43 (perfluoro cmpds, mostly C12), PF5070 (perfluoro cmpds, mostly C6)	298	350
	Caled Hydroclene	64742-88-7	100% aliphatic hydrocarbon	368	145
Low Flash Hydrocarbons[31]			Stoddard solvent and blends, mineral spirits C8 - C12 HC (similar to kerosene), contains benzene as contaminant	300 - 400	100 - 110
	Shellsol D40		mineral spirit aliphatic HC	300-415	104
Cyclic Volatile Methyl Siloxane	Green Earth® D5 (Dow Corning, GE, Shin-Etsu)	541-02-6	decamethylcyclopentasiloxane	410	171
Propylene Glycol Ethers	Solvair®	29911-28-2	dipropylene glycol n-butyl ether (DPnB) + biodegradable ingredients cleaner and liquid CO_2 rinsing and drying	446	212
	Rynex 3®	132739-31-2	substituted aliphatic glycol ethers; dipropylene glycol tert-butyl ether (DPTB)	419	>200
	Impress®, Gen-X	64742-48-9	Hydrocarbon (10 - 60%) + dipropylene glycol ether (10 - 50%)	368-414	154 -160
Acetal	Solvon K4	2568-90-3	1-(butoxymethoxy) butane (butylal)	357	144
Liquid Carbon Dioxide	Cool Clean Technologies, Inc., Solvair® (see above), and previously Micell Technologies	124-38-9	liquid carbon dioxide	-70 at 5.1 atm.	N/A

[31] Included here for reference only; low flash HC not evaluated as part of this alternatives assessment.

Category	Trade name	Solvent		Boiling Point (^oF)	Flash Point (^oF)
		CAS #	Chemical Name		
Supplemental Technology	GreenJet		mist of water and detergent	212	N/A
Wet Cleaning			water	212	N/A
Category	**Trade Name**	**Detergents and Additives**			
Wet Cleaning	Kreussler	106232-83-1	branched and linear alcohol ethoxylates		
		26027-37-2	oleic acid monoethanolamid, ethoxylated		
		69227-21-0	alcohols C12-C18 ethoxylated, propoxylated		
		112-34-5	2-(2-butoxyethoxy)ethanol		
		29923-31-7	sodium laurylglutamate		
		61791-32-0	glycine, N-[2-[(2-hydroxyethyl)amino]ethyl],N'-Cokos-acyl derivates, mono sodium salts		

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Assessment of Alternatives to Perchloroethylene for the Dry Cleaning Industry

About the Toxics Use Reduction Institute

The Toxics Use Reduction Institute (TURI) at the University of Massachusetts Lowell provides resources and tools to help Massachusetts businesses and communities make the Commonwealth a safer and more sustainable place to live and work. Established by the state's Toxics Use Reduction Act of 1989, TURI provides research, training, technical support, laboratory services and grant programs to reduce the use of toxic chemicals while enhancing the economic competitiveness of Massachusetts businesses. Learn more at www.turi.org.

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