Massachusetts Chemical Fact Sheet

Methylene Chloride

This fact sheet is part of a series of chemical fact sheets developed by TURI to help Massachusetts companies, community organizations and residents understand the chemical's use and health and environmental effects, as well as the availability of safer alternatives.

Overview

Methylene chloride, or dichloromethane (DCM), is a chlorinated solvent commonly used as a metal degreaser, a chemical intermediate, a reaction or extraction solvent, a paint stripper, and as a component in adhesives. Consumer products that can be purchased at local automotive and hardware stores, such as aerosol parts cleaners and paint strippers, may contain methylene chloride.

Methylene chloride exposure can result in serious adverse health effects including effects on the central nervous system, cardiovascular effects and possibly cancer. High, short-term exposures can be lethal. Its extreme volatility makes it especially dangerous, since unsafe airborne concentrations can be created readily through evaporation.

Methylene chloride is designated as a Higher Hazard Substance under the Toxics Use Reduction Act (TURA), which lowers the reporting threshold to 1,000 lb/year, effective January 2014.

Table 1. Methylene Chloride Facts

Synonyms	Dichloromethane (DCM), Methylene dichloride
Description	Colorless liquid with a sweet (chloroform-like) odor. Highly volatile at room temperature.
Chemical Formula	CH_2Cl_2
CAS Number	75-09-2
Vapor Pressure	349 mm Hg @ 68 °F (20 °C)
Vapor Density	2.93 (air = 1.02)
Flashpoint/ Flammability	Non-flammable
Combustibility	Reacts violently with oxidizing agents (such as perchlorates, peroxides, permanganates, chlorates, nitrates, chlorine, bromine and fluorine), chemically active metals (such as potassium, sodium, magnesium and aluminum), and strong bases (such as sodium hydroxide and potassium hydroxide).
Occupational Exposure Limits	**OSHA** Permissible Exposure Limit (PEL): 25 ppm* Short-term Exposure Limit (STEL): 125 ppm^ **NIOSH** Recommends that exposure to occupational carcinogens such as methylene chloride be limited to the lowest feasible concentration.
*8 hour time-weighted average; ^15 minutes	

Hazards

Acute (Short-Term) Health Effects

Methylene chloride is acutely toxic and deaths have occurred from using methylene chloride, most recently from paint stripping during bathtub refinishing, A number of deaths have been reported, including one in Massachusetts.[1]

Neurological. Exposure to methylene chloride can cause acute effects on brain function (central nervous system). Inhaling small amounts of methylene chloride can result in symptoms including difficulty with concentration and with tasks requiring hand-eye coordination.[2] Exposure to higher levels can result in dizziness, clumsiness, headache, nausea, tingling or numbness of fingers and toes.[2]

Respiratory. Inhaling methylene chloride can result in short-term respiratory effects, such as cough, loss of breath, chest tightness and asphyxiation.[2,3]

Eye, Nose, Throat and Skin. Inhaling higher levels of methylene chloride can irritate the nose, throat and lungs.[2] Skin exposure to methylene chloride is also irritating and can cause severe burns if the solvent sits on the skin.[2] Repeated skin exposure can cause dermatitis.[2]

Death. Over-exposure to methylene chloride has resulted in many fatalities.[2,3] Recently, deaths have occurred from using methylene chloride-containing paint stripping products in small, enclosed spaces with poor ventilation, such as during bathtub refinishing.[3,4,5]

Chronic (Long-Term) Health Effects

Cancer. The International Agency for Research on Cancer (IARC) classifies methylene chloride as a possible human carcinogen (Group 2B), and the US National Toxicology Program classifies it as "reasonably anticipated to be a human carcinogen."[6,7] Experimental carcinogenicity studies demonstrate that methylene chloride can cause lung, liver and mammary gland tumors.[8] Studies of methylene chloride exposure among workers indicate increased risk of lung, liver and breast cancer, and also provide evidence for an increased risk of additional types of cancer, including brain cancer, non-Hodgkin's lymphoma and multiple myeloma.[8,9]

Neurological. Effects on the nervous system can be long-lasting and possibly permanent if a person is exposed frequently to high levels of methylene chloride. Long-term effects can include fatigue, lack of muscle coordination, loss of concentration, short-term memory loss and personality changes, such as anxiety, nervousness or irritability.[2]

Organ Toxicity. Chronic exposure can cause damage to the liver and kidney.[2]

Cardiovascular. Methylene chloride is converted into carbon monoxide inside the body, impairing the delivery of oxygen. As a consequence, exposure to methylene chloride can worsen and cause additional symptoms of heart disease in those with a pre-existing condition.[2,10]

Reproductive/Developmental. Studies suggest that methylene chloride exposure during pregnancy can result in spontaneous abortion, other adverse effects on pregnancy, and decreased sperm count in men.[2] Methylene chloride can reach the fetus through the placenta and can enter breast milk.[2]

Additional chronic health concerns. Optic neuropathy (damage to the optic nerve) from exposure to methylene chloride has occurred, resulting in vision loss.[11]

While the acute and chronic effects reviewed above are primarily based on inhalation exposure, high levels of methylene chloride absorbed through the skin can cause similar effects.

Exposure Routes

If individuals using products containing methylene chloride can smell it, they are being overexposed. Methylene chloride cannot be smelled until the level in the air is 10 times higher than the Occupational Safety & Health Administration's (OSHA) 8-hour permissible exposure limit (PEL).[3] In addition, workers and others who routinely work with methylene chloride may become desensitized to the chemical odor, and may therefore be at greater risk of over-exposure via inhalation.

The highest exposures to methylene chloride usually occur in workplaces where the chemical is used in large volumes over long periods of time. However, high exposures can also occur when using small volumes of methylene chloride in confined spaces, such as in tank cleaning operations or in bathtub refinishing. Exposure can occur among workers using methylene chloride as well as among bystanders.[12] Occupational exposure to methylene chloride can occur during its manufacture, product formulation and production, packaging, shipping and handling.[7] Inhalation is the most significant route of exposure to methylene chloride in workplace settings.[13] However, dermal exposure can also be significant for individuals not using effective protective clothing, as required by OSHA under its Methylene Chloride Standard.[13]

Exposure to methylene chloride among the general public is also primarily through inhalation. Exposure can occur when using consumer products containing methylene chloride, such as paint removers, where use indoors can result in very high vapor concentrations. Air pollution is also a source of inhalation exposure of methylene chloride, especially for those living near hazardous waste sites.[7] Dermal exposure is also likely from consumer use of products, especially when working with paint stripping formulations or cleaning agents containing methylene chloride. Ingestion of methylene chloride is also possible, especially in areas where drinking water may be contaminated.

Exposure among the general public to methylene chloride in consumer products often occurs because many consumers are not aware that the most commonly used types of gloves, such as latex rubber and nitrile, are easily penetrated by methylene chloride.[14] Cartridge-type air purifying respirators and dust masks do not adequately protect against methylene chloride vapors.[3,14]

Methylene chloride evaporates very rapidly when sprayed, brushed or poured, and the vapors can quickly reach high concentrations in confined spaces.[3] Since methylene chloride vapors are heavier than air, vapors tend to concentrate near the ground; this can be particularly hazardous in tanks and tubs, small enclosed spaces, and for uses such as carpet adhesive where workers' breathing zone may be down low.[3,15] Exposure to as little as six ounces of methylene chloride-based material can be fatal.[3]

High Risk Populations

Because methylene chloride breaks down to form carbon monoxide (CO) in the body, those with preexisting heart and lung conditions are at greater risk from exposure to methylene chloride.[10] People who smoke already have higher levels of CO in the body and as a result, these individuals can experience the effects of methylene chloride at much lower levels.[2] People with lung conditions are also more sensitive to the health effects of methylene chloride. Hemoglobin in a developing fetus has a higher affinity for CO than an adult and thus the cardiovascular and neurotoxic effects of exposure to methylene chloride may be exacerbated.[16]

Children exposed to cancer-causing substances are more susceptible to developing cancer later in life.[17] Because methylene chloride is frequently found as a contaminant at hazardous waste sites, people living near these areas may be more at risk for exposure than the general public.

Environmental Fate and Transport

Because of its high vapor pressure, approximately 90% of methylene chloride that is released to the environment from both industrial and consumer uses will find its way into the atmosphere. The average atmospheric lifetime for methylene chloride is 130 days.[2] Environmental releases of methylene chloride to water will evaporate; the half-life measured in the laboratory is 21 minutes, yet the rate of volatilization in the environment will vary based on factors such as the pH of the water.[2] Methylene chloride is not expected to bioconcentrate; it has a low octanol/water partition coefficient (log $K_{ow,}$ 1.25).[2]

Use Nationally and in Massachusetts

> ***Massachusetts experienced a 54% decline in the use of methylene chloride from 1990 to 2010.***

In 2012, 261.5 million pounds of methylene chloride were produced and imported into the U.S.[12] Domestic demand in 2010 was estimated at 181 million pounds.[18] Methylene chloride is predominantly used as a solvent in a variety of industries and applications in the U.S. including:[19]

- Paint removal
- Adhesives
- Pharmaceutical manufacturing
- Metal cleaning
- Propellant blend in aerosols
- Chemical processing
- Flexible polyurethane foam manufacturing

Methylene chloride is also used as an extraction solvent in research and commercial laboratories.

A number of household products that can be purchased at hardware and automotive stores may contain methylene chloride. These include paint strippers, adhesives, varnishes, rust and spot removers, lubricants, valve cleaners and degreasers for automobiles. Methylene chloride has been used in the past in some pesticide products, but is no longer an active ingredient of any registered pesticide product in the U.S.[7]

Use in Massachusetts

Currently, the predominant uses of methylene chloride in Massachusetts follow national patterns and include use in: metal degreasing, paint stripping, adhesives and pharmaceutical preparation. The following information is based on use reporting to the TURA program:

- Businesses subject to TURA reported a 54% reduction in the use of methylene chloride from 1990 to 2012, from 7.8 million pounds in 1990 to 3.6 million pounds in 2012 (Figure 1).
- Eleven facilities reported using methylene chloride in 2012, a significant decrease from 47 facilities in 1990 (Table 2).
- Among the facilities reporting use in 1990 and 2012, use increased among two manufacturers of adhesives and sealants (ITW TACC and Key Polymer Corp).
- Three companies accounted for 75% of the reported use of methylene chloride in 2012: ITW TACC (manufacturer of adhesives and sealants containing methylene chloride), Houghton Chemical Co. (chemical distributor) and Savogran Co. (manufacturer of paint stripping products).

Many of the industries that used methylene chloride in the early years of the TURA program have subsequently redesigned their processes to reduce or eliminate use. In 2000, a survey of TURA facilities that reported using methylene chloride between 1995 and 1999 found that 15 of the 17 companies had either eliminated it, or reduced use to below reporting thresholds. Those that eliminated methylene chloride use did so primarily by identifying safer substitutes, such aqueous cleaning methods for degreasing operations, although some shifted to other solvents that also pose health concerns. The declines are most notable between 1994 and 1997 (Figure 1) and were likely driven in part by increased regulatory oversight of methylene chloride by both the U.S. Environmental Protection Agency (EPA) and OSHA.[20]

Some facilities that reported significant amounts of methylene chloride in the early years of the TURA program are no longer in operation, such as the Polaroid Corporation, which used methylene chloride in the production of film.

Figure 1. Methylene Chloride Use - TURA Program, 1990-2012

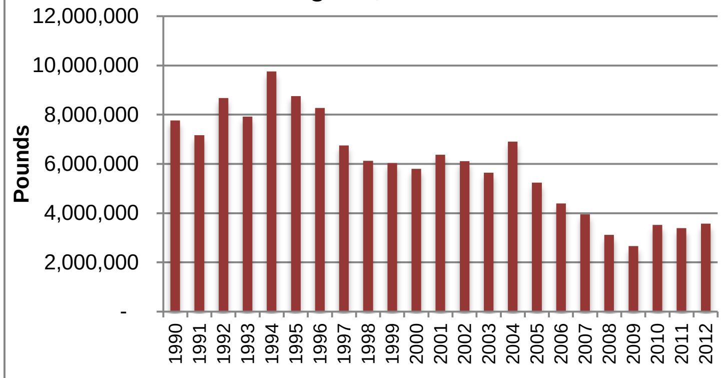
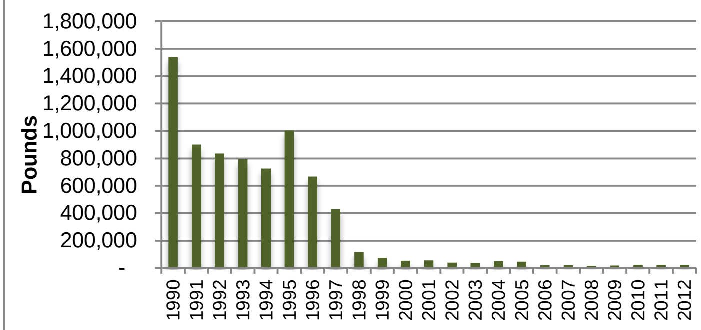


Figure 2: Methylene Chloride Environmental Releases - TURA Program, 1990-2012



Environmental Releases in Massachusetts

Massachusetts facilities also reported significant reductions in environmental releases of methylene chloride (Figure 2). From 1990-2010, releases declined 98%. Increased regulatory oversight of methylene chloride during the 1990s – including OSHA's 1997 methylene chloride rule that dramatically lowered occupational exposure limits for methylene chloride – contributed to the dramatic decline in environmental releases between 1997 and 1998.

Table 2: Summary of Methylene Chloride Use in Massachusetts

Industry Sector/Use	Facility Name	Location	Use (pounds) 1990	Use (pounds) 2012
Adhesives & sealants (7 facilities)	American Finish & Chemical Co	Chelsea	44,000	
	Bostik Findley Inc	Middleton	369,393	
	CL Hauthaway & Sons	Lynn	165,400	
	ITW TACC	Rockland	86,952	725,528
	Key Polymer Corp	Lawrence	61,000	129,166
	Koch Membrane Systems Inc	Wilmington	28,755	
	MODU Form Inc	Fitchburg	21,600	
Cleaning & degreasing (19 facilities)	Aerovox Inc	New Bedford	39,200	
	AGM Industries Inc	Canton	35,067	
	AW Chesterton Co	Woburn	11,000	
	Columbia Manufacturing Co	Westfield	103,183	
	CP Bourg	New Bedford	16,622	
	General Electric Co	Pittsfield	61,700	
	Globe Rubber Works	Rockland	20,142	
	Goddard Valve Corp	Worcester	14,400	
	International Equipment Co	Needham Heights	31,460	
	Invensys Systems Inc	Foxboro	60,885	
	Lucent Technologies Inc	North Andover	250,000	
	MA COM Inc	Burlington	10,711	
	MA COM Inc	Lowell	11,683	
	National Metal & Finishing Co	Springfield	18,600	
	Parker Hanafin Corp/Nichols Aircraft Div	Ayer	11,840	
	Precix Inc	New Bedford	29,975	
	Printed Circuit Corp	Woburn	107,804	
	Raytheon Co	Andover	71,285	
	Smith & Wesson	Springfield	33,275	
Chemical preparations (4 facilities)	Chemdesign Corp	Fitchburg	189,730	
	Printers Oil Supply	Wilmington	50,160	
	Shield Packaging	Dudley	74,855	
	Waters Corp	Taunton	12,380	
Printing ink (1 facility)	GEM Gravure Co Inc	Hanover	70,327	
Recycling and blending solvents (1 facility)	Safety Kleen	North Andover	1,506,178	
Paints & allied products (5 facilities)	Camger Chemical System	Norfolk	63,156	32,241
	Eastern Process Co	Hingham	27,108	
	Parks Corp	Somerset	416,745	
	Savogran Co	Norwood	1,468,445	1,170,191
	Sterling Clark Lurton	Malden	456,313	
Pharmaceutical preparations, diagnostic substances (3 facilities)	Johnson Matthey Pharma Serv Inc	Devens		99,890
	Johnson Matthey Pharma Serv Inc	North Andover		95,550
	PCI Synthesis Inc	Newburyport		50,783
Photographic equipment & supplies (4 facilities)	Electronic Concepts Inc	Lee	15,744	
	Polaroid Corp	Assonet	924,586	
	Polaroid Corp	Waltham	507,889	
	Polaroid Corp	Norwood	11,471	
Plastics & resins, plastic products, including foam products (5 facilities)	American Optical Corp	Southbridge	27,221	
	Emerson & Cuming Composites Material Inc	Canton	26,157	
	Ionics Inc	Watertown	91,400	
	Millipore Corp	Bedford	18,536	
Thread mills (1 facility)	New Bedford Thread Co Inc	Fairhaven	18,700	
Wholesale trade – chemicals & allied products* (5 facilities)	Astro Chemicals Inc	Springfield		315,340
	Callahan Co	Walpole		126,539
	Houghton Chemical Corp	Boston		779,344
	Monson Companies Inc	Leominster	75,170	
	Nexeo Solutions LLC	Tewksbury		50,715
		Total Methylene Chloride Use	***7,768,203***	***3,575,287***

*Data first reportable in 1991

Alternatives

There are a number of safer alternatives for methylene chloride used in various applications. For cleaning and stripping applications, please also see: www.cleanersolutions.org.

Paint Stripping

There are a wide variety of alternatives to methylene chloride based paint strippers. These include chemical alternatives as well as mechanical alternatives that loosen paint from surfaces.

Chemical Alternatives

Chemical-based paint strippers that are safer than methylene chloride, but do also present hazards, include: benzyl alcohol, propylene carbonate, dibasic esters (DBEs) (including dibasic adipate, dibasic glutamate or dibasic succinate, and their mixtures) and dimethyl sulfoxide (DMSO).

- Use of benzyl alcohol-based strippers may require replacing all metal equipment with polypropylene and composites, and masking off rubber parts before using. One recent evaluation concluded that benzyl alcohol-based paint strippers were the best performing alternatives to methylene chloride, yet the performance time is longer.[21] Benzyl alcohol is regulated as a volatile organic compound (VOC), and is a skin irritant.
- Dibasic esters and propylene carbonate can also be used as drop-in replacements, yet may require much more time to match the performance of methylene chloride.[21 22] Dibasic esters are eye irritants and individuals working with dibasic ester-based paint stripping products have reported blurred vision.[22]
- DMSO is considered to have low toxicity but has a high skin penetration rate. This enhances the risk of DMSO carrying other toxic constituents from the paint film into the body.[22]

While the above alternatives appear to be safer compared to methylene chloride, health effects have not been comprehensively investigated. Precautions need to be taken when using any chemical paint stripper, even if it is marketed as "safe" or "environmentally friendly." These include using only in well-ventilated areas and wearing appropriate protective clothing and eye wear, as well as continuing to seek safer alternatives.

Paint strippers containing n-methyl pyrrolidone (NMP) are not recommended due to reproductive toxicity concerns.[23] Some paint strippers based on dibasic esters may also contain NMP.

Process Alternatives

Alternatives to methylene chloride for dip tank paint stripping operations include caustic soda (sodium hydroxide) or potassium hydroxide. These formulations are extremely corrosive and can cause severe burns to the eyes and skin even upon brief contact. The acid-based solutions used for neutralization of spent tank contents are also corrosive, potentially causing skin burns, and may have additional toxicity concerns. Engineering controls can be used to minimize exposure to these corrosive solutions.

Other mechanical removal options exist, including media blasting and thermal stripping. Controlling exposure to sand blasting media is critical with this option; crystalline silica is a known carcinogen. Safer media, such as nut shells, plastic, sodium bicarbonate or steel shot, may be effective. There are some hazards from dust production. Thermal stripping devices should be used with caution because of the inherent fire risk and potential exposure to toxic emissions released as the paint is heated. Fire and emission hazards are significantly reduced when using steam rather than thermal paint stripping devices.

Additional process alternatives for methylene chloride-based paint stripping have been employed by the defense and aviation industries. These include the use of use of a xenon lamp combined with a continuous blasting stream of carbon dioxide pellets (Flashjet®).[24] This particular alternative may not be economically feasible for many facilities given high adoption cost and infrastructure requirements.[24] Additional abrasive stripping techniques using plastics, water and lasers have also been employed.[25] These alternatives are safer for human health compared to methylene chloride. However, environmental public health risks associated with dust production and paint waste migration are concerns with abrasive stripping techniques.

Metal Degreasing

Methylene chloride is used as a metal degreaser primarily in wipe cleaning applications (although it has historically been used as a vapor degreaser). Safer alternatives to solvent-based degreasing include aqueous and semi-aqueous processes, such as the use of soaking or ultrasonic equipment. Other alternatives for metal degreasing include hydrocarbon solvents, such as terpenes, alcohols, acetone, ketones and acetates. These options are generally less hazardous than methylene chloride but have health effects ranging from acute (e.g., eyes and respiratory irritation, dizziness, nausea, confusion) to chronic (e.g., liver and kidney problems). Many such solvents are also highly flammable.

Trichloroethylene (TCE) and n-propyl bromide (nPB) are unsuitable alternatives because of well-documented health effects including carcinogenicity, reproductive toxicity and neurotoxicity. Hydrochlorofluorocarbons pose ozone depletion hazards and hydrofluorocarbons pose global warming hazards. Other drop-in substitutes, such as hydrofluoroethers and volatile methyl siloxanes, can be effective but have been less studied in terms of their health and environmental impacts.

Adhesives

Alternatives to methylene chloride used as the solvent carrier in adhesive products include both non-solvent and solvent substitutes. Hot melt adhesives appear to be the least toxic alternative that are suitable for some, but not all, applications. Other non-solvent-based alternatives are available including aqueous-based carriers using latex or latex-synthetic blends.

However, there are worker sensitization concerns associated with latex and some aqueous carriers may contain ammonia, which can irritate the eyes, respiratory tract and skin. Additional process changes may be required if aqueous alternatives are used. For some applications, sewing or other mechanical attachment can replace the use of adhesives.

Some alternative solvent adhesive formulations use acetone. While they are generally lower in toxicity they have a very low flashpoint, so systems must be in place to minimize the chance of fire or explosion. Other alternative solvent-based formulations may contain mineral spirits, petroleum solvents, petroleum distillates and naphthas that present additional human health, environmental and/or safety concerns. Solvent-based formulations using nPB or TCE are undesirable alternatives to methylene chloride products given their significant human health and environmental health impacts.

Pharmaceutical Preparations & Research Laboratory Use

Alternatives are available for methylene chloride in laboratory research applications, including extractions and pharmaceutical preparations. For use in extracting organic compounds for trace analysis using gas chromatograph techniques, super critical CO_2 can be used. High costs for super critical CO_2 extraction technology limit its economic feasibility to mainly large users. Solid phase microextraction is an alternative process for extracting and analyzing trace organics that mitigates the need for methylene chloride.[26] Ethyl acetate is an effective replacement reaction or separation solvent for methylene chloride. While it has low toxicity, ethyl acetate is flammable and can be subject to hydrolysis.[27] Diethoxymethane is an effective alternative for methylene chloride as a reagent and process solvent, though it is flammable.[28] Current health data on diethoxymethane indicate low toxicity, but it has not been tested for chronic health effects.[27]

Alternatives for methylene chloride for additional research or laboratory applications will depend on solvent function needed.

Regulatory Context

Table 3: MASSACHUSETTS REGULATIONS & GUIDELINES	
Toxics Use Reduction Act	• Effective in reporting year 2014, methylene chloride designated as a Higher Hazard Substance and subject to reporting & planning requirements when more than 1,000 lb/year used.
Environmental & Public Health	• Subject to "Right to Know" requirements. • Ambient Air Guidelines: Threshold Effect Exposure Limit, 30 ppb; Ambient Air Limit, 20 ppb.
Waste Clean-up	• Under the MA Contingency Plan (MCP), a concentration of 0.1 µg/g in soil is considered protective of current and future uses of the remediated property. Other standards are also outlined under the MCP.

TABLE 4: OTHER STATE REGULATIONS (*Not Comprehensive*)	
California	• Regulated as a carcinogen under Proposition 65. • Methylene-based paint strippers proposed (2014) to be a Priority Product under the Safer Consumer Products regulation.

TABLE 5: U.S. REGULATIONS (*Not Comprehensive*)	
U.S. Safe Drinking Water Act	• Maximum Contaminant Level (MCL) in drinking water is 5 ppb.
U.S. RCRA	• Regulated as a hazardous waste.
U.S. Clean Air Act	• Listed as a Hazardous Air Pollutant and subject to several National Emission Standards for Hazardous Air Pollutants (NESHAPs), including standards for paint stripping. • Exempt from VOC regulations due to determination of negligible photochemical reactivity.
U.S. OSHA	• Permissible Exposure Limit (PEL): 25 ppm* • Short-term Exposure Limit (STEL): 125 ppm^
*8 hour time-weighted average; ^15 minutes	

Table 5: INTERNATIONAL REGULATIONS	
Canada	• Preparation and implementation of pollution prevention plans required under a notice in Part 4 of the Canadian Environmental Protection Act (2003).
European Union	• Domestic, professional and industrial use and marketing of methylene chloride-based paint strippers are severely restricted (Decision No 455/2009/EC). • European Trade Union includes methylene chloride on the Priority List for REACH Authorization. • The Swedish Chemical Products Ordinance of 1988 bans the sale of methylene chloride for consumer use.

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