

# Methyl Chloride: Handling, Storage, and Safety

Please use this guide in conjunction with this product's country-specific Safety Data Sheet (SDS) and the Safe Use conditions as described therein. Current Safety Data Sheets can be requested from Olin at info@olin.com.

Background	Methyl chloride is a clear, colorless gas. It has a faint, sweet odor that is noticeable only at levels that may be toxic. It is heavier than air and extremely flammable. It is stored and shipped under pressure.
	Nearly all of the methyl chloride produced is used as a raw material in the manufacture of other chemicals, including chloromethanes, silicone fluids and polymers, methyl cellulose, quaternary ammonium compounds, agricultural products, and butyl rubber.
	Olin ships methyl chloride in dedicated tank cars, tank trucks, and isocontainers.
Toxicity and Safe Handling	Please refer to the current Safety Data Sheet (SDS) prior to working with methyl chloride.
	Because methyl chloride is a colorless gas at room temperature with a mild odor only at toxic concentrations, it may pose a significant hazard to human health.
	Although liquid methyl chloride may produce frostbite-type burns upon skin contact, inhalation is the principal hazard. Initial symptoms of excessive inhalation exposure include lack of coordination and impaired judgment. High exposures may lead to uncoordinated movements, weakness, tremors, speech difficulties, and blurred vision. Gastrointestinal upset may occur with severe acute poisoning. Extreme exposures may cause convulsions, coma, or death.
	Any person showing or feeling the effects of inhaling methyl chloride should be removed to fresh air immediately and given prompt medical attention. A physician should be called or the person transported to a medical facility. If breathing stops, remove to fresh air, artificial respiration should be given, and oxygen should be administered by qualified personnel.
	Long-term exposure has been noted to cause kidney, liver, spleen, and testes effects in animals, and nervous system effects in humans. Repeated significant exposure to methyl chloride was also found to cause birth defects in animals and has been shown in animal studies to interfere with fertility in males. To minimize exposure to methyl chloride, adequate ventilation should be provided in the workplace. Exposure levels of methyl chloride vapor in the workplace atmosphere must be maintained below established occupational exposure limits (OEL). OEL's may vary by jurisdiction.

Exposure List <sup>3</sup>	Туре	Exposure Limit
Dow Industrial	TWA	25ppm
Hygiene Guideline <sup>1</sup>		
Dow Industrial	STEL	50ppm
Hygiene Guideline <sup>1</sup>		
ACGIH	TWA	50ppm
ACGIH	STEL	100ppm
US OSHA/Z2 <sup>2</sup>	TWA	100ppm
US OSHA/Z2	Ceiling	200ppm
US OSHA/Z2	Maximum	300ppm (5 min in any 3
	Concentration	hours)

The potential for dermal absorption of methyl chloride exists, including the mucous membranes and the eyes, either by contact with vapors or by direct skin contact.

1 Industrial Hygiene Guides (IHG) are Dow's internally-set occupational exposure guidelines (OEGs or aka: OELs). They are similar exposure guidelines set forth by regulatory bodies, but Dow's IHG's are not regulatory in nature. Olin Blue Cube Operations LLC currently follows Dow's Industrial Hygiene Guideline.

2 Occupational Safety and Hygiene Administration is a US federal agency that regulates the safety and health of workers in the USA; "Z2" regulates exposures to chemicals or hazardous substances in the workplace.
3 These are example exposure limits. Please refer to your SDS for specific occupational exposure limits, as exposure limits and relevant regulations may differ from the values listed depending on the jurisdiction.

Because of the lack of warning properties at levels approaching the exposure guidelines, it is recommended that a suitable method of continuous sampling and analysis of the work area be employed to ensure that the exposure guidelines are not exceeded. Monitoring of the work area air for methyl chloride contamination may be accomplished by suitable commercially available detection devices.

### Personal Protection

Workers should be thoroughly trained regarding the hazards of methyl chloride before starting any work involving this chemical. Persons working with methyl chloride should be provided with and instructed in the use of appropriate personal protective clothing and equipment, as required. Ventilation should be provided to control and maintain vapor concentrations below currently accepted OEL(s). In areas of insufficient ventilation or during emergency situations, self-contained, positive-pressure breathing apparatus approved by the National Institute of Occupational Safety and Health (NIOSH; provides technical research and guidance to the U.S. OSHA) should be used. Cartridge or canister type respirators are not recommended for use with methyl chloride.

The workplace should be equipped with readily accessible eye wash fountains and delugetype safety showers in the event of accidental eye or skin contact. If hand protection is needed, use an insulated glove for protection from liquid contact of the skin that may cause frostbite due to rapid cooling. When the potential for skin contact with liquid methyl chloride is a possibility, use of chemical protective gloves along with thermal gloves should be considered. Examples of preferred glove barrier materials include: Viton®, polyvinyl alcohol ("PVA") or ethyl vinyl alcohol laminate ("EVAL"). Examples of acceptable glove barrier materials include: Butyl rubber, Neoprene, and Nitrile/butadiene rubber ("nitrile" or "NBR").

Avoid gloves made of: Polyvinyl chloride ("PVC" or "vinyl"). Note: the selection of a specific glove for a particular application and duration of use in a workplace should also take into account all relevant workplace factors such as, but not limited to: other chemicals which may be handled, physical requirements (cut / puncture protection, dexterity, thermal protection), potential body reactions to glove materials, as well as the instructions / specifications provided by the glove supplier.

#### **Product Storage**

Each methyl chloride user is responsible for design and implementation of a storage and handling system that is suitable for their individual facility. Experience has shown that overexposure to methyl chloride is most likely to arise during storage, filling of transport equipment, handling and maintenance operations. Please read this section carefully.

#### Bulk Storage

Carbon-steel pressure tanks, designed according to the ASME Code for Unfired Pressure Vessels, are suitable for the bulk storage of methyl chloride. The storage tank should be designed for a minimum working pressure of 160 psig and equipped with a pressure-indicating device and dual safety valves set at the maximum allowable working pressure of the vessel. All piping should be Schedule 80, standard carbon steel that is welded throughout to eliminate screwed fittings. Differential pressure devices are suggested for level measurements.

Tanks should be located above ground in a limited access area away from buildings, thoroughfares, etc. Tanks should be equipped with a sprinkler, deluge monitor, or other fire suppression system. Spill containment for both the storage and unloading area should be designed to prevent spilled material from collecting under tanks, tank cars, or process lines.

All electrical wiring, fixtures, and equipment should be installed in accordance with the applicable national or local electrical standards, such as the U.S. National Electric Code for Class 1, Group D, Division 2 Hazardous Locations. Grounding of the methyl chloride system should be carefully planned and implemented to assure proper protection.

#### The Importance of Labeling

All transfer lines, piping and receiving containers should be properly labeled. The receiving tank should be identified and the appropriate safety and environmental information visible on all sides.

### **Product Transport** Tank Car Valves

The dome of a standard rail tank car (US DOT 105J300) contains three angle valves, a safety valve, and a magnetic gauging device (Figure 1). The two angle valves located along the main axis of the tank car are equipped with eduction lines extending to the bottom of the tank car and are used for unloading liquid methyl chloride. The angle valve, which is perpendicular to the axis of the tank car, terminates in the vapor space just under the dome.

The safety valve is set to discharge at 225 psig.



# **Product Transport** (continued)

### **Unloading Precautions**

Only experienced, thoroughly trained individuals, knowledgeable of the hazards associated with unloading, storing, and handling should attempt to unload methyl chloride. Written procedures should be developed and communicated to operating personnel prior to initiating any unloading operation. Olin suggests the following precautionary measures be addressed as a part of the unloading procedure.

- FLAMMABLE GAS placards should be prominently displayed to caution those in the area.
- The unloading spur should be electrically isolated from the rest of the rail line.
- The tank car and all transfer lines, liquid and vapor, should be adequately grounded before making any hose or piping connection to the rail car.
- A ground indicator light or alarm system should be used to verify grounding.
- Water deluge monitors or other fire suppression systems should be present.
- Non-sparking tools and protective clothing (safety glasses, hard hats, rubber-soled shoes) should be used.
- A safety shower and eye bath should be available close to the unloading platform.
- To avoid straining the angle valve, the non-sparking wrench used to remove and replace fittings should not exceed 18 inches in length.

### **Unloading Procedure**

Methyl chloride is unloaded as a liquid using a compressor. The preferred method of unloading is through a 2-inch, Schedule 80 steel pipe that is equipped with a check valve and a steel coupling or swivel joints. Flexible steel hose may also be used for unloading, although it may require more frequent inspection and maintenance.

Piping should be attached to one of the liquid angle valves in the tank car dome and to the methyl chloride storage tank. Additional piping should be connected to the gas angle valve in the dome, through a compressor equipped with a four-way valve arrangement and to the vapor line of the storage tank. All piping should include pressure gauges.



# **Product Transport** (continued)

To reduce the likelihood of contamination of the methyl chloride tank cars and the storage tank, the storage tank should be isolated from the process vent and recycle streams. The only connection between the process unit and the storage tank should be the methyl chloride feed line to the process. This line should be equipped with a check valve. It should also be closed when not transferring methyl chloride to the process.

After all the connections have been properly made, the liquid angle valve should be opened slowly and completely. If the valve is opened too quickly, the excess-flow valve will "seat" and methyl chloride will not flow. The excess-flow valve can be released by closing the liquid angle valve until the float in the excess-flow valve falls back into place. A click is heard when this occurs. Do not pound on the unloading valves or flanges to reseat the excess-flow valve, as this can result in premature failure of the equipment. Once the float falls, slowly open the angle valve again. This process should be repeated until the liquid valve is fully opened and the float remains in the "drop down" position.

Following the opening of the liquid angle valve, the gas valve should be opened and the compressor started. During unloading, the compressor is used to withdraw methyl chloride vapor from the top of the storage tank and pump it into the top of the tank car. This forces liquid methyl chloride from the car into the storage tank.

The level detection device in the storage tank or a liquid sensing probe in the unloading line should be used to determine when the car is empty. The tank car magnetic gauging device does not reach the bottom of the tank car and cannot be used to determine when the car is empty.

When all of the liquid has been pushed out of the tank car, the compressor should be used to remove most of the vapor remaining in the car. To reduce air infiltration and the potential for developing an explosive mixture in the empty tank car, a small amount of methyl chloride vapor, sufficient to maintain a slight positive pressure (5 psig), should be allowed to remain in the car.

After the car has been emptied, the liquid and gas angle valves should be closed. The unloading lines should then be removed, the angle valves plugged and the dome cover closed and sealed with the Olin-provided seal for car return.

**Product Handling** Important information on proper handling procedures for methyl chloride is presented below.

Specific recommendations are presented for:

- Flammability of methyl chloride; and
- Disposal of solvents and waste.

#### Flammability of Methyl Chloride

Methyl chloride is a flammable gas. Its lower and upper flammable limits are 8.1% and 17.4% in air, respectively. Under some conditions, methyl chloride may burn with a nearly invisible flame and hence provides no advance warning of the presence of a fire.

Smoking and carrying matches or lighters should be prohibited in areas where methyl chloride is stored, handled, or used. Only under the provisions of a special permit, issued when the area has been tested and found to be free of methyl chloride or other flammables, should open flames or spark-producing devices be permitted

Product Handling (continued)	Buildings should be well ventilated and protected by automatic sprinkler systems. Carbon dioxide and dry chemical extinguishers are suitable for fighting methyl chloride fires.	
	Consult Olin's safety data sheet (SDS) for additional information regarding fire- fighting measures	
	<b>Disposal of Waste</b> Never dispose of waste by pouring it on the ground, down a sewer or into a septic system. Methyl chloride should be disposed of in a licensed, permitted incinerator or other thermal destruction device. Be sure to review all applicable laws and regulations before disposing of methyl chloride wastes.	
Decomposition Hazards	In the presence of moisture, methyl chloride may slowly hydrolyze to form hydrochloric acid.	
	Decomposition products depend upon temperature, air supply, and the presence of other materials. Decomposition products can include, but are not limited to, hydrogen chloride and phosgene.	
Materials of Construction	Dry methyl chloride can be used safely with most common metals except aluminum, magnesium and sodium. Aluminum must be avoided, since flammable methyl aluminum compounds may be formed.	
	Carbon steel is the most common material used in methyl chloride service.	
	In the presence of moisture, methyl chloride may slowly hydrolyze to form hydrochloric acid, this will attack carbon steel and even stainless steel.	
	Natural rubber and most neoprene rubbers are unsuitable for methyl chloride service. Teflon™ or Chemraz® elastomers may provide suitable service in a liquid system. Viton™ fluoroelastomer may be of value in a vapor system. All valving and piping gaskets should be of "fire-safe" design.	
Spills, Leaks, and Disposal	Methyl chloride may damage the environment if released into the air, water or soil. You should be aware of the potential effects of methyl chloride on the environment before beginning to use them for any application. Wherever possible, you should employ engineering controls and management practices to ensure that the product is utilized in the most environmentally responsible manner possible.	
	General Safety Guidelines to Prevent Water, Soil and Air Contamination	
	Minimize the number of transfer processes.	
	<ul> <li>Steel piping, couplings, and swivel joints are preferred whenever transferring methyl chloride. Flexible stainless steel hoses may be used but require more frequent inspections.</li> </ul>	
	Connect fittings securely before performing transfer operations.	
	<ul> <li>Be aware of residual amounts of methyl chloride in transfer lines. If possible, purge all lines with nitrogen before disassembling or disconnecting.</li> </ul>	
	<ul> <li>Implement a proven dry-disconnect coupling, or purge and cap lines and hoses to prevent contamination.</li> </ul>	

## Spills, Leaks, and Disposal (continued)

#### Avoid high-risk situations

Practical experience has shown that the risk of soil or groundwater contamination is particularly high in the following situations:

- Overfilling storage containers and not containing the excess liquid.
- Failing to notice or repair minor leaks in pumps, pipes, hoses, couplings or other equipment.

### Personal precautions, protective equipment and emergency procedures:

- Evacuate area. Keep personnel out of low areas.
- Keep upwind of spill. Ventilate area of leak or spill.
- Stop flow of gas. Isolate area until gas has dispersed.
- No smoking in area. Eliminate all sources of ignition in vicinity of spill or released vapor to avoid fire or explosion.
- Ground and bond all containers and handling equipment.
- Only trained and properly protected personnel must be involved in clean-up operations. Use appropriate safety equipment. For additional information, refer to Section 8 of the Safety Data Sheet (Exposure Controls and Personal Protection).
- For large spills, warn public of downwind explosion hazard.
- Check area with combustible gas detector before reentering area.
- Spills of this liquefied gas may form ice, which can plug drains and can make valves inoperable.
- Contact of water with liquefied gas can result in boiling, frothing, and rapid generation of vapor.

## Physical Properties

Molecular Weight	50.5 g/mol	
Specific Gravity, 25/25 °C	0.92	
Freezing Point	-98 °C	
Boiling Point, at 760 mm Hg,	-23.8 °C	
Vapor Pressure at 20 °C,	3730 mm Hg	
Specific Heat at 20 °C	Liquid 0.38	Sat vapor 0.23
Heat of Vaporization, @ 20 °C	91.3 cal/gm	
Flash Point	-45 °C	
Flammable Limits (in air)	Lower (LFL) 8.1%	
	Upper (UFL)	
Critical Temperature	143.1 °C	
Critical Pressure	50101 mmHg	
Critical Volume	2.76 cc/gm	
Critical Compressibility Factor	0.269	
Acentric Factor	0.1514	
Solubility, at 760 mmHg, 20 °C, g/100g	(Solvent in H <sub>2</sub> 0) 0.74	(H <sub>2</sub> 0 in Solvent) 0.24





# Heat of Vaporization

















# **Surface Tension**

## Saturated Vapor Density

Saturated Vapor Density of Methyl Chloride 30000 Vapor Pressure, mmHg 25000 20000 15000 10000 5000 0 0.001 0.003 0.006 0.011 0.019 0.031 0.050 0.077 Density, g/cc





# Thermal Conductivity

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Product Stewardship	At Olin, our Product Stewardship program is guided by our core values – Act with Integr Drive Innovation and Improvement, and Lift Olin People. We are committed to the s handling and use of our products – and enabling all of our collaborators throughout value chain to do the same. As a responsible corporate citizen and certified RC14001®:2015, we assess our products' safety, health, and environmental informat and take appropriate steps to protect employees, public health, and the environment Ultimately, our product stewardship program's success rests with each individual involve with Olin products – from the initial concept and research to the manufacture, sat distribution, use, disposal, and recycling of each product.	
Regulatory Datasheets (RDS)	Olin Corporation provides information on the regulatory status of its products under prominent regulatory programs in the Regulatory Datasheet (RDS).	

Regulatory Datasheets can be requested from Olin at info@olin.com.

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