Chloroform: 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@olinbc.com.

Background

Chloroform is a clear, colorless, nonflammable liquid that has a mild odor. Its main use is as a chemical intermediate in the manufacture of hydrochlorofluorocarbon 22 (chlorodifluoromethane, or ‘HCFC-22’), which is primarily a refrigerant and feedstock for fluoropolymers. Chloroform also has minor applications as a process solvent in the production of some pharmaceuticals and agricultural products.

Toxicity and Safe Handling

Please refer to the current Safety Data Sheet (SDS) prior to working with chloroform.

Due to chloroform’s volatility, inhalation is the principal hazard, but the liquid is also toxic if ingested. Reactions to an excessive inhalation exposure include headache, dizziness, drunkenness, nausea, and loss of consciousness. Excessive exposure can cause systemic injury to the kidneys and liver. Extremely high levels may increase myocardial irritability (irregular heartbeats) and can cause death.

The likelihood and degree of the injury may be increased by the use of alcohol before or after exposure to chloroform.

Any person showing or feeling the effects of inhaling chloroform should be removed to fresh air immediately and given prompt medical attention. If breathing stops, mouth-to-mouth resuscitation should be given.

Adequate ventilation should be provided in the workplace to minimize the possibility of an inhalation hazard.

Exposure levels of chloroform vapor in the workplace atmosphere must be maintained below established occupational exposure limits (OEL). The ACGIH TLV is 10 ppm (TWA), and the US OSHA OEL is 50 ppm (Ceiling). OEL’S may vary by jurisdiction.

The odor threshold of chloroform is 85 ppm1.

Vapors of chloroform are heavier than air and will collect in low areas. Handling and storage areas (depressions, pits, basements, etc.), located below grade can create potential hazard due to the accumulation of vapors.

Personal Protection

Persons working with chloroform 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 with insufficient ventilation or during emergency situations, self-contained, positive-pressure-breathing apparatus approved by the National Institute of Occupational Safety and Health (NIOSH) should be used. Cartridge or canister-type respirators are not recommended for use with chloroform.

The workplace should be equipped with readily accessible eye wash fountains and deluge-type safety showers in the event of accidental eye or skin contact. If hand protection is needed, gloves made of impervious materials such as polyvinyl alcohol, Viton®, or nitrile rubber should be worn.

Product Storage

Experience has shown that overexposure to chlorinated solvents is most likely to arise during storage, filling, handling and maintenance operations. Please read this section carefully, as it will provide you with the proper procedures for working with chloroform.

Drum Storage

Chlorinated solvents are often delivered in drums or other returnable containers. On arrival, store these containers in an area equipped for spill and leakage containment or over a sump that is isolated from sewer/septic or groundwater releases. The system should be large enough to contain the full potential volume of material in primary storage. Such containment areas should not have bottom outlets and should be made of solvent-resistant material. Cover storage sites for holding containers of chlorinated solvents to protect them from direct exposure to sunlight and rain.

You should review and follow all laws and regulations governing the use of solvent-resistant materials and solvent-tight containers for storage facilities. Never use ordinary concrete alone when constructing drum storage areas because chlorinated solvents can permeate concrete. Instead, a common recommendation is to use painted mild steel to allow observers to verify the integrity of the storage area.

Bulk Storage

Carbon-steel tanks are usually adequate for storing chlorinated solvents, although you should note that the build-up of moisture inside these tanks may lead to corrosion problems. If you require exceptional solvent purity, stainless steel may be used or tanks may be coated with a solvent-resistant lining.

Equipment used in handling, storing or processing chlorinated solvents, including tanks, pumps, piping, valves, meters and other instrumentation, must not contain aluminum, or other white metals, such as magnesium or zinc. The possibility of a reaction between these metals and the solvent may cause corrosion and could ultimately cause equipment failure.
Product Storage (continued)

Tank Specifications
Tank specifications should be in accordance with all applicable laws and regulations. Chloroform has a specific gravity greater than 1 (water = 1), which should be reflected in tank design.

- Ensure tanks are clean, dry and free from rust
- Ensure tanks have appropriate pressure-vacuum relief valves, a vent dryer or inert gas pad, and optimal vapor return lines for transfer operations
- Use closed-loop filling systems with a vapor return line between delivery and storage vessels. Vapor return is also advised for in-process filling operations.
- Ensure tanks are grounded to prevent the build-up of static electricity

Tank Cleaning, Repair and Maintenance
Practice continuous maintenance on your tanks to prevent loss of solvent.

Thoroughly trained personnel who are familiar with the hazards, appropriate safety precautions, equipment, and first aid procedures applicable to working with chlorinated solvents should direct tank cleaning. In some areas, applicable laws and regulations may require that cleaning, repair and maintenance work be performed by certified companies only. All equipment should be maintained and serviced according to the manufacturer's recommendations.

Because solvents can evaporate rapidly, a small leak under pressure can result in the loss of solvent without the warning of a pool of liquid. A simple halide leak detector can be used to check connections, valves, pump packing and any other accessible parts of the system. Be sure that all connections are made with a material that will not react with the solvent. Polytetrafluoroethylene (PTFE or Teflon™) tape is recommended to wrap screwed fitting threads before assembly.

Solvent Sampling
Visual inspection does not always detect moisture and other contaminants. Consider these recommended procedures when sampling:

- Dry bottles before taking samples.
- Sample bottles should be narrow-mouthed glass (preferably amber color) and be filled almost to the shoulder of the bottle. Completely filling sample bottles can result in broken containers due to thermal expansion.
- Label bottles.
- Bottle caps should be of a type that will seal against the neck of the bottle. Conical cap liners made of polyethylene work well, as do flat liners made of soft Teflon or foamed polyethylene
- Store samples in tightly sealed secondary containers in a cool place and away from direct sunlight, or properly dispose of samples after testing.
- Transport and store samples in appropriately sized secondary containers.

The best method of obtaining samples from delivered tank cars and tank trucks is from a sample point on the unloading line. Take the sample when the line is full of liquid and before off-loading the product into a storage vessel.

When sampling from storage tanks, withdraw samples from the center of the tank, away from the bottom or sides of the tank. To do this, insert the sampling device into the top of the tank or collect the sample from a drain on piping to or from an operating recirculation pump.
Product Storage (continued)

Unloading Bulk Solvent
Properly trained and equipped personnel, who are present at all times, should carry out unloading operations in areas that are contained, or at least protected, with a solvent-resistant material. Whenever a container is unloaded by gravity or pump, a vapor piping system should connect between the shipping container and the receiving tank to reduce solvent losses.

The preferred method, and that with the greatest control, is unloading from the bottom of the shipping container with a pump, rather than by gravity. If pumping facilities are not available and the tank relief devices have a sufficiently high rating (check the maximum allowable pressure), the contents may be unloaded through a dip tube with gas pressure applied into the top of the tank. Connect the inert gas line to the top of the tank using a pressure control valve and a pressure relief device set at 50% of the tank relief valve set pressure. Clean, dry nitrogen at a pressure of 20-30 psig (1034-1551 mmHg gauge) is suitable for this purpose.

Do not use air pressure because moisture in the air could contaminate the solvent.
Other important information:
- Ensure the receiving tank has adequate capacity.
- Set air valves and vapor return lines prior to beginning pumping operations.
- The use of dedicated unloading hoses is preferred. If these are not available, the transfer hose must be cleaned before use.
  - At the beginning of the transfer, flush the hoses with a small amount of solvent for cleaning purposes and collect it for waste disposal.
  - After the flush, a sample of the solvent may be taken into a glass container for analysis.
  - Repeat flushing as necessary until the hose is clean and you obtain an uncontaminated solvent sample.
- When unloading is complete, collect all solvent drained from hoses, valves, etc., for use or disposal.

Direct transfer from bulk delivery vessels into drums is NOT recommended.
Customers who receive bulk quantities of chloroform and repackage them into 55-gallon drums or other small volume containers should first unload the solvent from the delivery vessel into a stationary bulk storage tank and then drum from the storage tank. Make sure that all fittings and transfer operations take place in an area protected with safety and environmental controls to provide adequate ventilation and to prevent spills and solvent contamination.

When it is not possible to use a stationary bulk tank, appropriate equipment, including pump and valves, must be in place between the truck and drumming station. Provide secondary containment for both the truck and drumming station and follow all other general unloading procedures.
**Product Storage (continued)**

**The Importance of Labeling**

When you transfer a chlorinated solvent from its original container, properly label the new container. The contents of the new container should be identified and the safety and environmental information shown on the original label from the Olin packaging should be visible. If the containers will be exported, the language on the label should be understandable by the receiving party.

**Secondary Containment**

To help prevent soil and groundwater contamination, a secondary containment system is strongly recommended and in many countries is a legal requirement. Always consult local regulations for requirements which may be more detailed or restrictive than the following general information.

Secondary containment systems may take the form of a dual-walled container, a dike around the tank area or a sump below the tank area. The system should be designed specifically for the chemicals being handled and it should be constructed from solvent-resistant material. In addition, the system should be large enough to contain the full potential volume of material in primary storage vessel/container. Drains to a collection point must be installed and must be independent of the sewage/drainage system for external discharge already located at the site.

**Storage of Spent Solvents**

The storage of spent solvents requires the same precautions as the storage of fresh solvents.

**Product Handling**

Important information on proper handling procedures for chloroform is presented below. Specific recommendations are presented for:

- Transferring solvents from storage;
- Storage of spent solvents; and
- Disposal of solvents and waste.

**Disposal of Spent Solvents and Waste**

Use an authorized processor or a special waste treatment plant to dispose of distillation residues and water contaminated with chloroform.

Never dispose of chloroform waste by pouring it on the ground, down a sewer or into a septic system. Dow also strongly discourages the disposal of chloroform wastes in landfills. This practice is illegal in most countries. In addition, the wastes from different solvents should never be mixed, even in disposal. Doing so would make reclamation and recycling impractical. And, in some countries, such mixing is illegal. Be sure to review all applicable laws and regulations before disposing of chlorinated solvent wastes.
**Decomposition Hazards**

Chloroform decomposes very slowly upon prolonged exposure to sunlight or air. Small amounts of inhibitors, usually 2-methyl-2-butene or ethyl alcohol, are added to stabilize it against decomposition in storage. In the presence of strong alkalis, chloroform may react violently. It also reacts with aluminum.

Chloroform may thermally decompose upon exposure to open flames or high-temperature surfaces. Operating and handling areas should be kept free of open flames, welding arcs, or other high-temperature sources that may induce solvent decomposition. Involvement of chloroform in a fire can result in the formation of hydrogen chloride and phosgene. Do not use chloroform as a fire extinguishing medium.

**Materials of Construction**

Dry chloroform does not react with most commonly used construction materials, such as iron and steel. It reacts very slowly with copper and lead. It is not compatible, however, with easily oxidized nonferrous metals, such as aluminum and magnesium. Do not use containers, pumps, lines, or equipment made of nonferrous metals for handling, shipping, or storing chloroform.

**Spills, Leaks, and Disposal**

Chloroform may damage the environment if released into the air, water or soil. You should be aware of the potential effects chloroform on the environment before beginning to use them for any application. The following guidelines are a checklist for both health and environmental safety. Wherever possible, you should employ engineering controls and management practices to ensure that the solvent is utilized in the most environmentally responsible manner possible.

**General Safety Guidelines to Prevent Water, Soil and Air Contamination**

- Cover chloroform containers when not in use
- Minimize the number of transfer processes
- Use nozzles, hoses and couplings whenever transferring solvent
- Connect hoses securely before performing filling operations
- When moving drums from one location to another, use a mobile trough that is large enough to hold the contents of the drum in the event of a leak
- Be aware of residual amounts of solvent in pipes and hoses. If possible, purge all lines and hoses, with air or nitrogen before disassembling or disconnecting
- Implement a proven dry-disconnect coupling, or purge and cap lines and hoses to prevent contamination. Capping hoses that contain residual liquid solvent is not recommended as the hose may rupture if the solvent heats up and expands.
- Whenever possible, install permanent piping for applications which involve frequent filling and emptying procedures
- Conduct all solvent operations in contained areas that are coated with solvent-resistant materials that can accommodate the volumes being handled and isolated from drains to the sewer or ground.

**Prevent and Reduce Air Contamination**

Chloroform has a relatively short lifetime in the atmosphere.

When not in use, cover openings in equipment and vessels (tanks, drums, etc.) that contain chloroform to minimize release of solvent vapors into the workplace. Most facilities that use chloroform are equipped with exhaust systems that reduce human exposure to solvent vapors. However, the exhaust should be treated to remove the solvent vapors before they are released into the atmosphere.
Several exhaust purification methods are available. Carbon adsorption is the traditional method to capture solvent vapors. The exhaust gasses are passed through a bed of activated carbon which adsorbs the solvent vapors. Studies show that polymeric beds are also very effective at this. Refer to Olin’s technical data sheet, “Polymeric Adsorption Systems For Solvents” for more information.

De-sorption and recovery processes are critical parts of the overall process. The traditional use of steam to recover solvents from can generate a considerable amount of water that needs to be treated or decontaminated. Alternative processes use heat and condensation to recover the solvent, with less stabilizer loss and no additional waste stream to treat.

For more information on recommended technologies and suppliers for chloroform vent abatement/recovery, contact Olin at info@olinbc.com.

Prevent and Reduce Water and Soil Contamination
Chloroform is not "readily biodegradable" according to the definition by the Organization for Economic Cooperation and Development (OECD). Thus, contamination of groundwater and soil by chlorinated solvents can be a serious problem.

Chloroform is not very soluble in water, but it can still cause contamination of surface or groundwater. Additionally, because chloroform is heavier than water, large spills will tend to collect at low points, creating a concentrated source for continuing contamination. Even process water that has come in contact with chloroform will contain some of the substance and should be handled as a hazardous waste stream.

The main causes of groundwater and soil contamination are negligence and improper storage, handling, and disposal procedures. Contaminated soil and water is both difficult and costly to clean. Therefore, avoiding leaks and spills that can cause groundwater and soil contamination is imperative. Do not dispose of contaminated water in the sewer or septic system, or pour it on the ground.

Furthermore, those responsible for handling chloroform and its waste must understand and follow approved procedures and relevant governmental regulations for the handling and disposal of chloroform and the waste. Laws dictating how a user may treat hazardous waste will vary. We recommend that you contact a licensed disposal contractor to handle any waste, contamination or disposal situations. If you intend to treat any contaminated material onsite, we recommend that you contact a qualified environmental engineering company to assist with the permitting and design of any such system.

Avoid high-risk situations
- Practical experience has shown that the risk of soil or groundwater contamination is particularly high in the following situations:
- Transferring or pumping chloroform to and from drums and small containers when leaks and spills are not properly prevented and/or contained
- Disregarding the amounts of residual solvent in containers you assume to be "empty"
- Overfilling storage containers and not containing the excess liquid
- Disregarding the amounts of residual solvent left in hoses and allowing it to drip onto unprotected ground
- Failing to notice or repair minor leaks in pumps, pipes, hoses, couplings or other equipment.
Spills, Leaks, and Disposal (continued)

- Carrying chloroform in open containers and disregarding minor spills
- Carelessness when storing or handling wastes contaminated with chlorinated solvents
- Spills or leaks of chloroform require prompt containment and clean up, followed by careful disposal of the recovered material. In the event of a spill or leak:
  - Remove all unnecessary personnel from the area.
  - Ventilate the area thoroughly.
  - Clean-up personnel must wear NIOSH-approved, self-contained, positive-pressure, breathing apparatus.
  - Contain and soak up the liquid with an absorbent.
  - Transfer the absorbed material to closed metal containers and dispose of properly.

When disposing of waste chloroform, the preferred options are to send the material to a licensed reclaimer or to a permitted incinerator. Any disposal practice must be in compliance with federal, state, and local regulations. Do not dump into sewers, on the ground, or into any body of water.

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<td>Boiling Point, at 760 mm Hg, °C</td>
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<td>Vapor Pressure at 20°C, mm Hg</td>
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<td>Heat of Vaporization, cal/g</td>
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<td>Solubility, at 20°C, g/100g</td>
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Vapor Pressure

Chloroform Vapor Pressure

![Chloroform Vapor Pressure Graph]

0.00  10.00  100.00  1000.00  10000.00

Vapor Pressure, mmHg

0  10  20  30  40  50  60  70  80  90  100

Temperature, °C
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