

## CHLORINATED SOLVENTS

## PRODUCT STEWARDSHIP MANUAL





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## **Abbreviations**

ACGIH	American Conference of Governmental Industrial Hygienists		
ASTM	American Society for Testing Materials		
ECSA	European Chlorinated Solvents Association		
EPA	Environmental Protection Agency		
EU	European Union		
GHS	Globally Harmonized System		
GWP	Global Warming Potential		
HCFC	Hydrochlorofluorocarbon		
HFC	Hydrofluorocarbon		
HSIA	Halogenated Solvents Industry Alliance		
IARC	International Agency for Research on Cancer		
LD50	Lethal Dose 50%		
MAK	Maximum Allowable Concentration		
MEC	Methylene Chloride		
MIR	Maximum Incremental Reactivity		
NIOSH	National Institute of Occupational Safety and Health		
NTP	National Toxicology Program		
ODP	Ozone Depletion Potential		
OECD	Organization for Economic Cooperation and Development		
OEL	Occupational Exposure Limit		
PCE	Perchloroethylene		
PPE	Personal Protective Equipment		
PTFE	Polytetrafluoroethylene		
PVA	Polyvinyl Alcohol		
RoC	Report on Carcinogens		
SCBA	Self-Contained Breathing Apparatus		
SCOEL	Scientific Committee on Occupational Exposure Limits		
SDS	Safety Data Sheet		
TCA	Trichloroacetic Acid		
TLV	Threshold Limit Value		
TWA	Time Weighted Average (8-hour)		
VOC	Volatile Organic Compounds		

## **Introduction**



At Olin, our Product Stewardship program is guided by our core values – Act with Integrity, Drive Innovation and Improvement, and Lift Olin People. We are committed to the safe handling and use of our products – and enabling all of our collaborators throughout the value chain to do the same. As a responsible corporate citizen, we assess our products' safety, health, and environmental information and take appropriate steps to protect employees, public health, and the environment. Ultimately, our product stewardship program's success rests with each individual involved with Olin products – from the initial concept and research to the manufacture, sale, distribution, use, disposal, and recycling of each product.

### Purpose of This Manual

This manual is designed to help you safeguard the health of your employees, encourage safe working practices, maintain chlorinated solvent exposure levels at or below the current industrial health limits, and protect the environment. It is essential that everyone who comes into contact with chlorinated solvents is thoroughly trained in safe work practices and the proper use of equipment. All personnel should be aware of potential hazards, understand what and how to use personal protective equipment, and know how to seek medical assistance and/or administer first aid.

Further, Olin recommends that every individual who handles, stores, or is regularly exposed to chlorinated solvents, read and familiarize themselves with the contents of this manual and the appropriate Safety Data Sheets (SDS). Every individual who may use these solvents is required to know how to access and understand the information contained in the SDS.

### Safety Data Sheets

Each SDS contains information for handling specific Olin chlorinated solvents. Always consult the appropriate SDS or contact Olin to make sure you have the proper chlorinated solvent for your application. For the most current SDS please contact us at info@olin.com.

## Solvents Covered in This Manual

While this manual outlines general safety information for methylene chloride and perchloroethylene products, the same principles apply to other chlorinated organic products produced by Olin.

Some grades of chlorinated solvents are designed for particular applications and may contain stabilizers that have been developed with specific end uses in mind; therefore, they may not be suitable for other applications. Consult the relevant SDS or contact Olin to decide on the right product for your end-use requirements. Also, be aware of changing marketplace conditions and government regulations that may restrict the products available to you.

KEEP THIS MANUAL AND THE CURRENT SDS NEARBY IN CASE OF EMERGENCY AND AS A USEFUL REFERENCE.

## **Product Stewardship**



# A Commitment to Health, Safety, and the Environment

This section discusses Olin's Product Stewardship philosophy, including:

- The role of the end user
- Guidelines for using chlorinated solvents
- · Special considerations for methylene chloride and perchloroethylene
- · Information about Safety Data Sheets

Chlorinated solvents have been widely used for metal cleaning, urethane foam blowing, pharmaceutical manufacturing, cleaning printed circuit board components, and dry cleaning for more than 50 years. They are also used as feedstocks for the manufacture of fluorocarbons, refrigerants and blowing agents (HCFCs and HFCs), and other industrial products.

Olin is committed to assessing safety, health, and environmental information on our products, and then taking appropriate steps to protect employee and public health, and the environment. Olin has devoted resources to promoting the safe and effective use of chlorinated solvents, as well as their proper storage and disposal.

#### Hazard vs. Risk

It is important to properly define the words "hazard" and "risk." Hazard refers to the intrinsic toxicological and ecotoxicological properties of a substance that have potential to cause harm to humans and/or the environment. Risk incorporates an estimate of the potential exposure to these hazards. Risk is a function of both exposure and hazard; with no exposure, there is no risk. Whether a hazardous substance poses a risk depends on the circumstances under which the substance is used or handled. For example, the likelihood of exposure to humans or the environment is reduced when a hazardous substance is used in a closed system, thereby reducing risk.

### You Have a Role in Product Stewardship

In general, Product Stewardship is a way of assessing information on the health and environmental aspects of a product and then providing guidelines to protect the environment and those who use the product. At Olin, Product Stewardship is a process to make health, safety and environmental protection an integral part of designing, manufacturing, marketing, distributing, using, recycling, and disposing of products.

Government regulations vary by location and are subject to change. It is ultimately your responsibility to ensure that your use of chlorinated solvents complies with all applicable regulations, and that the application of these solvents meets all national, regional, and local regulations.

### **End-Use Guidelines**

Always review how you plan to use chlorinated solvents before choosing one for your application.

Olin recommends you use the following end-use guidelines as part of the process of evaluating applications for chlorinated solvents.

#### Olin's chlorinated solvents should not be used in applications where:

- Soil or groundwater contamination is likely (direct application to the ground, sink drains, sewers, or septic tanks).
- Overexposure is likely (small rooms or confined spaces where inadequate ventilation exists and no adequate personal protective equipment (PPE) is available and in use).
- Skin contact is likely (such as removing adhesive tape from the skin, or as a hand cleaner to remove oils and greases).
- Direct contact with food is possible.
- Vapor concentrations are used in the lammable range without appropriate control equipment.
- Disposal of waste would pose an environmental or health risk.
- Chemical reactivity poses a danger (contact with strong alkali or in areas where welding is done).
- · Any applicable regulation would be violated.

## Product Stewardship - Continued

## Sensitive Uses: Tobacco Products

Olin will not knowingly sell or sample any product or service ("Product") into any commercial or developmental application that is intended for the tobacco industry, directly or indirectly, for use in the production of tobacco, the manufacture of tobacco products, manufacture of electronic cigarettes and similar devices (i.e., electronic nicotine delivery systems (ENDS)), or the manufacture of marijuana products intended for human consumption.

Olin prohibits the use of its products in the synthesis or the final formulation of illegal drugs.

#### Exemptions:

- Olin products used in tobacco product packaging that is not intended for human consumption. As long as the packaging is not consumed as part of the product use.
- Insecticides and Pesticides whose active ingredients have been registered for use in the production of tobacco or marijuana by the local authority, if required, and one of the following regulatory authorities in the United States, the European Union, the United Kingdom, Germany, France, Spain, Italy, Japan, Australia, or Canada.
- Products used for general industrial purposes that are not intended to come into contact with the tobacco products.

## Sensitive Uses: Medical And Pharma Applications

Olin will not knowingly sell or sample any product or service ("Product") into any commercial or developmental application that is intended for: a. Permanent or long-term contact with internal body fluids or internal body tissues. Long term is a use which exceeds 72 continuous hours, b. Use in cardiac prosthetic devices regardless of the length of time involved (cardiac prosthetic devices include, but are not limited to, pacemaker leads and devices, artificial hearts, heart valves, intra-aortic balloons and control systems and ventricular bypass assisted devices); c. Use as a critical component in medical devices that support or sustain human life; or

d. Use specifically by pregnant women or in applications designed specifically to promote or interfere with human reproduction.

### All Products intended for use in pharmaceutical applications must pass the then current Pharmaceutical Liability Guidelines and requires written approval by Olin.

Pharmaceutical applications are defined as the provision of a medicinal substance or a drug other than a nutrient with the intent to bypass or to alter or restore normal in vivo synthesis, metabolic or physiologic state. Olin does not endorse or claim suitability of its products for specific medical applications. It is the responsibility of the medical device or pharmaceutical manufacturer to determine that the Olin product is safe, lawful, and technically suitable for the intended use.

Olin makes no warranties, express or implied, concerning the suitability of any Olin product for use in medical applications.

## Sensitive Uses: Products/Articles Intended For Use By Individuals Of Sensitive Populations

Olin makes no warranties, express or implied, concerning the suitability of any Olin products to be used to produce consumer products or articles intended for use by individuals of sensitive populations such as children, the elderly, or are likely to come in regular close contact with children, childcare settings, or the elderly.

#### Chlorinated solvents have been used effectively in a variety of applications over many years. Olin today supports the following applications:

- Aerosol products formulation (only perchloroethylene and methylene chloride for certain applications outside the EU)
- · Chemical processing industry
- Coatings and adhesives formulation
- Dry cleaning

- Fluorocarbon production
- Metal cleaning/degreasing
- Paint formulation
- Pharmaceuticals
   manufacturing
- Silicone production
- · Urethane foam blowing

Olin is continuously reviewing the applications in which chlorinated solvents are used, especially in light of new regulations and other potential restrictions that may be placed on the use of these solvents.

Olin restricts the use of chlorinated solvents in certain end-use applications. Please contact your local Olin sales representative for more information. The use of chlorinated solvents in aerosol applications should be carefully considered by the formulator to minimize the potential for human or environmental exposures in end-use applications.

There may be other applications that are not appropriate for these chlorinated solvents. The use of certain chlorinated solvents is restricted under certain national or regional regulations. Always consult the appropriate SDS or contact Olin to make sure you have the appropriate chlorinated solvent for your application.

Methylene chloride and perchloroethylene can be used safely in many applications. Exposure can be adequately controlled through ventilation, engineering controls, work practices, and personal protective equipment (PPE). Review each application carefully to ensure that exposures are below established limits.

## Safety Data Sheets

### Always review the SDS before handling chlorinated solvents.

Never handle any chlorinated solvent before you have read the relevant SDS. Each SDS contains information for handling a specific Olin chlorinated solvent. SDSs are updated regularly and reflect the most current detailed information on health effects, handling precautions, and first aid. They may also provide additional information that is not contained in this manual.

The SDS must be readily accessible to all persons where the product is being used. It is your responsibility to ensure that the most up-to-date SDS, provided by the supplier, is available to, and understood by, all employees who work with chlorinated solvents.

For details on the general physical properties of chlorinated solvents, the selection of solvents, equipment for specific end uses, and general use, refer to the back cover of this manual for the phone number, web address, and mailing address of an Olin office in your region. Be sure to ask for literature or other materials appropriate to your specific application.

## Human Health Considerations



This section presents important information about keeping individuals safe when working with chlorinated solvents. In this section, you will find general safety information, along with specific recommendations for:

- Personal protective equipment (PPE)
- Monitoring solvent vapor levels
- Entry guidelines for tanks, pits, and other confined areas

### **Toxicity and Risk**

Essentially all substances, both natural and man-made, are toxic to some degree. Toxicity is defined as the ability of a substance to produce any harmful effect to a living organism, at some level or frequency of exposure, by inhalation, ingestion, or direct skin or eye contact.

Risk is determined by exposure and hazard. Thus, the potential risk of a hazardous substance can be considerably reduced with proper handling, such as the use of engineering controls, fume hoods, respirators, chemical goggles, and other safety equipment, all of which limit exposure. At recommended occupational exposure levels (see appropriate SDS), it is unlikely that chlorinated solvents would produce adverse effects, even from repeated exposure. Used properly by trained personnel and stored carefully in accordance with applicable laws and regulations, chlorinated solvents can be used safely and provide effective solutions for your solvent needs.

Experience has shown that overexposure to chlorinated solvents is most likely to arise during storage, filling, handling, and maintenance operations. Please read these sections carefully, as they will provide you with the proper guidelines for working with chlorinated solvents.

### Exposure

It is important to distinguish between short-term exposure (acute effects) and long-term exposure (chronic effects). Route of exposure is also an important consideration that is addressed later.

#### Short-Term Exposure

Acute (short-term) exposure to chlorinated solvents above the recommended exposure guidelines can have effects on the central nervous system (light-headedness, drowsiness, headache, giddiness). Typically these effects are reversible, and behavioral and neurological studies have not shown any significant irreversible effects in humans from short-term exposures. Higher concentrations can cause anesthetic or narcotic effects.

Prolonged or repeated exposure to high concentrations may lead to unconsciousness or, in extreme circumstances, prove fatal. At very high exposure levels, chlorinated solvents can sensitize the heart to the effects of adrenaline and similar agents, which may lead to sudden cardiac arrest. Chlorinated solvents may irritate the respiratory tract (at very high concentrations).

Acute exposure to high concentrations of perchloroethylene can also lead to irreversible alterations in human liver function or to effects on the kidneys, although the latter is less well documented in humans than in laboratory animals. Very high exposures to methylene chloride can increase levels of carboxyhemoglobin and reduce oxygenation capacity of hemoglobin, which can be fatal.

## Human Health Considerations - Continued

### Table 1: OELs and Odor Thresholds

Solvent	Occupational Exposure Limits <sup>1</sup>	Odor Threshold	Slight (not unpleasant)	Strong (unpleasant)
Methylene Chloride	ACGIH TLV 50 ppm TWA EU SCOEL: 100 ppm	250 ppm	250 – 1,000 ppm	> 1,000 ppm
Perchloroethylene	ACGIH TLV 25 ppm TWA EU SCOEL: 20 ppm	5 – 70 ppm	100 – 200 ppm	> 280 ppm

<sup>1</sup> These are example exposure limits current at time of publication of this manual. Please refer to your country-specific SDS for current occupational exposure limits as applicable to your region and application.

#### Long-Term Exposure

Many studies have been conducted in laboratory animals to assess the potential effects of long-term exposure to chlorinated solvents. Typically, these studies evaluate a wide range of exposures by the oral and/or inhalation route over the lifetime of the test animals, to discern the potential for toxicity to major organ systems (immune system, respiratory, renal, circulatory, etc.) and development of tumors following chronic repeated exposure. Often the induction of tumors in laboratory animals requires a lifetime of chronic, daily, high level exposures. Mechanistic data are used to understand the similarities and differences between laboratory animals and humans with respect to exposure and organ system toxicity and induction of tumors. Human epidemiology data are used to help understand the relevance of the effects seen in laboratory animal studies and risks to humans. With chlorinated solvents, as with most industrial chemicals, high dose effects in seen in laboratory animals may not be relevant with respect to real world exposures of humans in the workplace.

Occupational Exposure Limits (OELs) are workplace exposure limits derived to protect against developing adverse health effects associated with both acute and chronic exposure. Workers should consult the SDS for awareness of any potential health effects from workplace exposure, current OELs for the substances with which they are exposed, and with their Industrial Hygienist for specific guidance on safe work practices within their organization.

## **Routes of Exposure**

When considering the toxicity of chlorinated solvents, the route of exposure is important. The likely routes of workplace exposure are inhalation, ingestion, or direct contact with the skin or eyes.

See Table 2 for a summary of the acute health effects of methylene chloride and perchloroethylene. For specific safety information, refer to the appropriate SDS.

### Inhalation

Inhalation of solvent vapor is the most likely route of exposure to chlorinated solvents. Therefore, it is essential to keep ambient levels in the workplace at or below the regulated or recommended occupational exposure standards. The developed OELs and TLVs reflect maximum average airborne concentrations of a hazardous material to which healthy adult workers can be exposed during an 8-hour workday and 40-hour week over a working lifetime without experiencing significant adverse health effects (Table 1). Groups such as the German Maximum Allowable Concentration (MAK) Commission, American Conference of Governmental Industrial Hygienists (ACGIH), and the EU Scientific Committee on Occupational Exposure Limits (SCOEL) are independent, non-regulatory organizations. These groups have developed MAK and Threshold Limit Value (TLV) guidelines to assist professionals in the control of health hazards in the workplace. Industrial hygiene professionals around the world refer to these guidelines. Please contact Olin at <u>info@olin.com</u> for guidance in relation to your jurisdiction. For additional information on first aid measures for inhalation, see the First Aid section of this manual.

#### **Odor Threshold**

Solvent vapors in the air produce various intensities of odor. The characteristic smell of chlorinated solvents has been described as "sweetish," "aromatic" or "ether-like." The odor threshold values are different for the solvents (see Table 1) covered in this manual. Although smell by itself is not adequate as a warning of overexposure, it is clear indication of a condition that needs further investigation. Individuals can become accustomed or insensitive to the odor. Therefore, the perception of odor is not an adequate warning of excessive exposure. To ensure employee safety, a trained individual should monitor the work area regularly with appropriate monitoring methods.

#### Ingestion

Swallowing small amounts of chlorinated solvents incidental to normal handling operations is not likely to cause injury. Swallowing larger amounts, either accidentally or intentionally, could result in serious injury or death. Do not eat, drink, or smoke in areas where chlorinated solvents are stored or used.

One way to compare the acute oral toxicity of substances is to determine their LD50. The LD50 is the single oral dose, expressed in grams per kilogram of body weight, which results in a 50 % mortality rate in laboratory animals. The oral LD50s of the chlorinated solvents are relatively high (grams per kg body weight), which generally indicates a low degree of acute oral toxicity.

#### Skin Contact

Skin contact should be avoided for all chlorinated solvents addressed in this manual, as described in more detail below. Appropriate handling precautions and proper use of PPE should be employed to prevent skin contact.

## Human Health Considerations - Continued

Brief skin contact with methylene chloride may cause moderate skin irritation with local redness, and drying and flaking of the skin. The response may be more severe on covered skin (under clothing, or gloves). Prolonged skin contact with methylene chloride may cause skin burns. Symptoms may include pain, severe local redness, swelling, and tissue damage. Prolonged skin contact may cause drying and flaking of the skin. Single prolonged skin exposure is unlikely to result in absorption of harmful amounts.

Brief skin contact with perchloroethylene may cause moderate skin irritation with local redness. Repeated skin contact with perchloroethylene may cause skin burns. Symptoms may include pain, severe local redness, swelling, and tissue damage. Prolonged skin contact may cause drying and flaking of the skin. Single prolonged skin exposure is unlikely to result in absorption of harmful amounts. However, perchloroethylene is classified as a dermal sensitizer based on animal data, therefore any skin contact should be avoided and chemical-resistant gloves should be worn.

Chlorinated solvents can defat the skin. This may allow infection and dermatitis to develop, especially where there is substantial daily contact. Chlorinated solvents can also cause irritation if the affected skin is prone to rubbing against shoes, clothing, or gloves. Methylene chloride may cause more significant skin irritation than perchloroethylene (see Table 2), while perchloroethylene is classified as a dermal sensitizer based on animal data.

### Eye Contact

All chlorinated solvents can cause eye irritation to varying degrees, therefore exposure to the eyes should be avoided with appropriate handling precautions and proper PPE. Low vapor concentrations may cause eye irritation; these concentrations are easily attainable at room temperature if vaporization is not properly controlled.

Methylene chloride may cause moderate eye irritation that may be slow to heal and may cause slight corneal injury. Exposure to methylene chloride vapors may cause eye irritation experienced as mild discomfort and redness. If liquid methylene chloride comes into contact with the eyes, immediately flush eyes with water for five minutes, remove contact lenses (if present), and continue flushing for an additional 15 minutes. Obtain medical attention without delay, preferably from an ophthalmologist.

Perchloroethylene may cause slight eye irritation. Exposure to perchloroethylene may cause pain disproportionate to the level of irritation to eye tissues. Low vapor concentrations may cause eye irritation; these concentrations are easily attainable at room temperature. If liquid perchloroethylene comes into contact with the eyes, flush eyes thoroughly with water for one to two minutes, remove contact lenses (if present) and continue flushing for several additional minutes. If effects occur, consult a physician, preferably an ophthalmologist.

### Table 2: Summary of Potential Health Effects in Humans from Acute Exposure to Chlorinated Solvents

	Central Nervous System Effects <sup>1</sup>	Eye Irritation <sup>2</sup>	Skin Irritation <sup>3</sup>
Methylene chloride	> 200 ppm vapor	> 500 ppm vapor	Moderate
Perchloroethylene	> 100 ppm vapor	> 100 ppm vapor	Slight to Moderate

<sup>1</sup> For example: headache, dizziness, sleepiness. Usually these effects are reversible if the person is removed from the area and given fresh air. <sup>2</sup> Painful.

<sup>3</sup> Effects become more severe on covered skin (under clothing, gloves) and upon prolonged or repeated exposure. All chlorinated solvents can cause defatting of the skin with repeated exposure.

## **General Safety/First Aid**



## **General Safety Guidelines**

- Always consult the appropriate SDS before beginning work and keep it nearby so you can refer to it in case of an accident or exposure.
- Know which type of solvent and grade you are handling, and be aware of its properties and hazards.
- Always use the appropriate PPE and safety equipment for the application. Wear protective garments, chemical-resistant gloves, and eye protection at all times.
- **Be alert.** When working with chlorinated solvents, avoid situations that can result in overexposure.
- Monitor the air regularly for the presence of chlorinated solvents. *Do not rely on smell alone as an indicator of hazardous exposure levels* (see Table 1 on page 8). Odor is not an adequate warning signal for potential overexposure.
- Trained personnel should regularly monitor solvent concentrations in the air to ensure safety and to comply with all applicable regulations.
- **Do not drink alcohol** before working with chlorinated solvents or after possible overexposure. Alcohol consumption in an industrial workplace is unwise, dangerous, and often illegal. Alcohol consumption may accentuate the central nervous system symptoms associated with overexposure to chlorinated solvents, and may lower your tolerance to adverse effects caused by inhaling solvent vapor.
- Avoid contact with your skin. Prolonged or repeated contact of chlorinated solvents with the skin may cause irritation. Certain inhibitors in some products and certain chlorinated solvent products may cause skin sensitization.

### First Aid

- Immediately seek fresh air and assistance if you become lightheaded while working with chlorinated solvents; dizziness and loss of coordination can lead to more serious accidents.
- If inhaled, move person to fresh air. If not breathing, give artificial respiration; if by mouth to mouth, use rescuer protection (pocket mask, etc.). If breathing is difficult, oxygen should be administered by qualified personnel. Call a physician or transport to a medical facility.
- If skin contact does occur, wash the skin immediately and thoroughly with water.
- In case of eye contact, immediately flush eyes with water, remove contact lenses, if present, and continue flushing for an additional 15 minutes. Obtain medical attention, preferably from an ophthalmologist.
- If ingestion occurs, do not induce vomiting. Call a physician and/ or take the employee to an emergency medical facility. If the solvent liquid enters the lungs, it may be rapidly absorbed by the lung tissue, leading to injury of other body systems.

## Safe Handling/Exposure Control



## **Personal Protective Equipment**

Do not work in areas contaminated by solvent vapor unless you are properly equipped and trained. You must have appropriate protective equipment and use it in accordance with the manufacturer's instructions and all applicable regulations. Protect yourself and safeguard the health and safety of operators, maintenance employees, and all others who work with chlorinated solvents.

### Eye Baths and Showers

Ensure that eye baths and showers are readily available for emergency use and that access routes to these facilities are free of obstructions. Regularly test eye baths and showers for proper operation, including temperature and adequate water flow.

#### What to Wear

When handling chlorinated solvents, wear:

- Protective clothing chemically resistant to this material. Selection of specific items such as face shield, boots, apron, or full body suit will depend on the task.
- Safety glasses with side shields (or their equivalent), or chemical goggles, when working in situations where the solvent may splash.
- Respiratory protection in case of likely overexposure (or have appropriate ventilation).
- Impervious gloves made from resistant materials. When determining which type of gloves to use, it is important to verify what type of solvent you are handling and how long the gloves will be exposed (see Appendix B).

The following additional protective equipment may be indicated for maintenance personnel:

- · Chemical goggles or face shield.
- Rescue harness and lifeline for entering tanks and other enclosed or confined spaces.
- Positive-pressure air-line masks with proper reduction valves and filters, or self-contained, positive-pressure breathing apparatus. **NOTE: Never use an industrial cartridge respirator for entry into tanks or other confined spaces.** Approved industrial respirators should only be used for temporary emergency use, such as escaping from contaminated areas. They also should not be used as a substitute for adequate ventilation or proper equipment operation.

#### **Protective Equipment Maintenance**

It is important to maintain and service all equipment according to manufacturers' recommendations. Conduct regular practice drills using personal protective equipment (PPE) to make sure equipment fits properly, hoses are secure, etc. All respiratory protection programs must conform to applicable occupational safety and health requirements.

## Monitoring Solvent Vapor Levels

There are several ways of measuring the concentration of chlorinated solvents in the air; however, special training is needed to ensure that the measurements are reliable and meaningful. Therefore, make sure that solvent vapor levels are checked regularly by trained specialists.

## Safe Handling/Exposure Control - Continued

### **Direct Exposure Measurements**

The simplest method for performing spot measurements is to use a commercially available colorimetric device, such as a Draeger tube or an MSA/Auer tube. These devices give only spot measurements, and can be affected at times by humidity or by other chemicals present in the air, making results difficult to interpret. Sophisticated instruments for continuous measurement of solvent vapors—such as infrared spectrometers, flame ionization detectors or photo ionization detectors—are also available; however special training is required to become proficient with their use. Always read the instructions carefully before using any detection device.

#### Indirect Exposure Measurements

Indirect exposure measurements are more accurate than direct methods. The most common indirect devices (vapor monitoring badges and personal monitoring pumps) sample a known quantity of air either by diffusion or drawing through a tube containing activated carbon. A laboratory analyzes the carbon to determine the contaminants present and measure their concentrations.

This method also tends to be the most accurate, and is valid in the range of ACGIH or TLV concentration values (National Institute of Occupational Safety and Health—NIOSH method 1003).

# Entry Guidelines for Tanks, Pits, and Other Confined Areas

Confined-area entry is the most hazardous operation involving chlorinated solvents. Chlorinated solvent vapors are heavier than air, and high concentrations can collect in low, confined and unventilated spaces such as tanks or pits. It is therefore important to keep the tank ventilated and use appropriate respiratory protection during the entire cleaning or repair operation. The tank should be ventilated through openings at the bottom and top of the tank, or exhausted mechanically from the lowest point in the confined area.

Additionally, the oxygen level in the tank should be measured by oxygen meter before and during any entry into the confined area. **Oxygen levels should never fall below 19.5 percent.** 

A common industrial cartridge respirator **does not** provide protection if oxygen levels are too low. Failure to use supplied air respirators (Self-Contained Breathing Apparatus (SCBA) or air line respirator) when entering confined or unventilated areas is dangerous. Very high vapor concentrations combined with insufficient oxygen levels can cause dizziness, loss of coordination, unconsciousness, even death.

Individuals who are familiar with the hazards, appropriate safety precautions, equipment, and rescue and first aid guidelines associated with the use of chlorinated solvents should supervise tank and pit cleaning operations (see the sections on The Supervisor's Role and Observers, on this page).

### General Tank-Entry Guidelines

- 1. Obtain written permission to enter the tank.
- 2. Lock out power feeds.
- 3. Shut off heating systems.

- 4. Drain solvent.
- 5. Disconnect all pipelines, including vents into or out of the tank; cap pipe ends; or install a blank in the pipeline.
- 6. Air-dry the tank.
- 7. Vent solvent vapors properly.
- Monitor the air in the area/ vessel to ensure that the oxygen concentration is sufficient and the solvent vapors are at acceptable levels for the respirator/PPE.
- 9. Display "Employee in Tank" signs at all entry points.
- 10. Have a person wearing proper PPE stationed outside the tank as an observer.
- 11. Follow all applicable regulations for confined-area entry.

#### The Supervisor's Role

The crew supervisor should carefully inspect the tank before cleaning or repair operations begin. Make certain that manholes are easily accessible, brightly illuminated, and large enough to accommodate safety gear. Steps and ladders must be rigid and well secured. If possible, provide mechanical hoisting equipment in the event it becomes necessary to evacuate injured or disabled employees.

The supervisor should also make sure that all employees entering the tank or serving as observers have the necessary, chemical-resistant protective equipment. Check the fit, operation, and suitability of all safety equipment, clothing, and breathing equipment.

#### Observers

Station a fully equipped observer outside the tank at all times. He or she must be capable of performing rescue guidelines.

If you are the observer outside the tank, stay alert. Watch for signs of overexposure (nausea, dizziness, loss of inhibitions, giddiness, or loss of coordination) in both the employee in the tank and yourself. Make sure that other employees are within calling distance, and that a notification guideline is in place.

### **Additional Information**

More information on confined-area entry is available from relevant regulatory authorities and from national publications on confined spaces such as the ASTM Standard Practice for Confined Area Entry.<sup>1</sup>

<sup>1</sup>In the U.S., information is available from American Society for Testing Materials (ASTM): ASTM Standard Practice for Confined Area Entry, D-4276. Contact ASTM at www.astm. org, or ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959. In the UK, the Health and Safety Executive has a publication called "Confined Spaces, A brief guide to working safely." Other jurisdictions have varying legislation on confined spaces and this should be confirmed with national regulatory authorities.



## Safe Handling/Exposure Control - Continued

## Proper Handling Related to Heat

### Keep Solvents Away From Flames and Heat

Do not use or store chlorinated solvents near open flames or excessive heat (such as ovens, furnaces, space heaters, welding operations, and pilot lights). When solvent vapors are exposed to extreme heat, they can decompose, yielding highly corrosive or toxic products such as hydrogen chloride, carbon dioxide, carbon monoxide, and chlorine, which can create greater hazards than the solvent itself, including metal corrosion in the workplace and toxicity to employees. Under certain conditions such as welding, very low levels of phosgene may form (see Figure 1).

### **Detecting Decomposition Products**

If methylene chloride or perchloroethylene decomposes, dangerous concentrations of phosgene can sometimes build up before the hydrogen chloride or chlorine level is high enough for individuals to notice.

**Do not rely on smell alone.** Hydrogen chloride and chlorine are strong respiratory irritants. If you are experiencing eye, nose, or throat irritation, leave the area immediately.

Figure 1: Levels of Hydrogen Chloride, Chlorine, and Phosgene When Welding in the Presence of Chlorinated Organics



<sup>1</sup>Range of solvent concentrations in test vessel.

<sup>1</sup>Range of solvent concentrations in test vessel

Hydrogen chloride, chlorine, and phosgene are classified as toxic inhalation hazards. Conduct a job safety assessment to identify tasks, potential hazards, recommended guidelines, personal protective equipment, and training necessary for situations where these substances may be present or formed. If processes involving extreme heat, such as welding operations, must be conducted in an area where chlorinated solvents may be present, ensure that there will be adequate ventilation, and test regularly for phosgene. If acceptable levels cannot be achieved, any employees in that area should wear a positive-pressure breathing apparatus.

Do not smoke while handling chlorinated solvents or in areas where they are present.

### **Proper Ventilation**

If hot processes are unavoidable in areas where solvent vapors are present, the products of combustion should be vented outside the building through corrosion-resistant ducts. The air supply for space heaters, ovens, or furnaces should never be drawn from areas containing solvent vapor. For example, they should not have their intakes located near exhaust vents that carry solvent vapor.

### Welding and Torch-Cutting

**Do not weld** in any area where chlorinated solvent vapors may exist. Avoid arc welding near equipment containing these solvents, because air currents may direct vapors toward the welding operation.

Furthermore, **do not weld** any drum that has previously contained chlorinated solvents. The concentration of residual vapors in the drum might be in a flammable range and could cause an explosion (see Table 3).

The special precautions that apply to welding also apply to torch-cutting. **Do not torch-cut** any drum that has previously contained chlorinated solvents. Do not torch-cut in an area where solvent vapors may be present, because of flammability and solvent decomposition.

### Table 3: Flammable Limits in Air

Volume % of Solvent in Air at 25 °C (77 °F)			
	Upper Flammable Limit (UFL)	Lower Flammable Limit (LFL)	
Methylene Chloride	22	14	
Perchloroethylene	None	None	

NOTES: (1) See the Safety Data Sheets for product-specific information. (2) Mixtures of chlorinated solvents with other substances, or in different atmospheres, may alter the flammability limits given above.

## **Environmental Considerations**



## Release to the Atmosphere

#### Stratospheric Ozone Depletion

Methylene chloride and perchloroethylene have not been implicated in stratospheric ozone depletion. Their relatively short atmospheric lifetimes indicate they are destroyed in the troposphere and have negligible effect on the stratospheric chlorine load.

#### Tropospheric Ozone Formation (Photochemical Smog)

#### Volatile Organic Compounds (VOCs) Regulations United States

Methylene chloride and perchloroethylene do not contribute significantly to tropospheric ozone formation. Methylene chloride and perchloroethylene are both exempt under the U.S. EPA Regulations for VOCs.\*

#### Europe

Methylene chloride and perchloroethylene have a vapor pressure above 0.01 kPa at 20 °C, and are therefore considered as VOCs according to the definition of the European Industrial Emissions Directive (2010/75/ EU). For applications defined in the European Industrial Emissions Directive, the rules laid out in national legislation which implements this directive must be followed.\*\*

#### **Climate Change**

Greenhouse gases like carbon dioxide are believed to contribute to global warming by absorbing thermal radiation emitted by the earth. Methylene chloride and perchloroethylene have short atmospheric lifetimes, and exist at extremely low concentrations. As a result, their contribution to global warming is very low (see Table 4).

#### Acid Rain

Human contribution to acid rain includes the burning of fossil fuels, which release oxides of sulfur and nitrogen. The quantities of chlorinated solvents released into the atmosphere are insignificant compared with the amounts of these oxides produced. Chlorinated solvents are estimated to contribute to significantly less than one percent of the acid rain produced through human activities (see Table 4).

### Additional Information

To find more information about chlorinated solvents, or to request the most current version of the Chlorinated Solvents Product Stewardship Manual, please contact us at <u>info@olin.com</u> or:

- www.hsia.org
- <u>www.chlorinatedsolvents.org</u> (ECSA)
- <u>www.Olin.com</u>

#### Table 4: Environmental Properties of Chlorinated Solvents

	Ozone Global Depletion Potential (ODP) <sup>a1</sup>	Maximum Warming Potential (GWP) <sup>a2</sup>	Contribution Incremental Reactivity (MIR) <sup>3</sup>	Atmospheric to Acid Rain	Lifetime
Methylene chloride	~ 0	9	0.07	<< 1%	5-6 months
Perchloroethylene	~ 0	Not Available	0.04	<< 1%	5-6 months

FR-2009-06-23/html/E9-14580.htm.

<sup>a</sup> Relative to  $CO_2$  (100 years); where  $CO_2$  = 1

Kurylo, M.J. and Rodriguez, J. M. (1998) Chapter 2: Short-Lived Compounds. Scientific Assessment of Ozone Depletion: 1998. World Meteorological Organization (NOAA, et al.).
 Myhre G. and Shindell D. (lead authors) and 36 others, Anthropogenic and Natural Radiative Forcing, Ch. 8 of Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate FINAL 09 November 2017 18 Change [Stocker, T.F. et al. (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp.

<sup>3</sup>CEPA/CARB (2006) Regulation for Reducing the Ozone Formed from Aerosol Coating Product Emissions. Aerosol Coating Products (Section 94520-94528, Title 17, Division 3, Chapter 1, Subchapter 8.5, Article 3). California Environmental Protection Agency, Air Resources Board.

\*These solvents are exempt from U.S. EPA regulations for VOC except for specific use categories, where MIR-based reactivity rules apply. For more information, consult the U.S. Federal Register Volume 74, Number 119, Pages 29595-29607, (6/23/2009), website: www.gpo.gov/fdsys/pkg

\*\*In EU release to atmosphere is regulated via the Industrial Emissions Directive 2010/75/EU

## **Environmental Emission Control**



This section presents important information on how to prevent environmental contamination when working with chlorinated solvents. Specific recommendations are presented for preventing and reducing contamination to air, soil, and water.

Chlorinated solvents may damage the environment if they are released into the air, water, or soil. You should be aware of the potential effects of chlorinated solvents 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. In applications such as metal cleaning and dry cleaning, releases into the atmosphere can be dramatically reduced by using modern, closed machines or vent recovery systems that utilize activated carbon.

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

- Cover chlorinated solvent 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.
- Utilize 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 that involve frequent filling and emptying.
- Conduct all solvent operations in containment areas that are coated with solvent-resistant materials and that can accommodate the volumes being handled, and isolated from drains to the sewer or ground (see Secondary Containment, page 19).

### Prevent and Reduce Air Contamination

Chlorinated solvents have a relatively short lifetime in the atmosphere. The atmospheric lifetime of methylene chloride and perchloroethylene is only a few months (see Table 4 on page 14).

When they are not in use, cover openings in equipment and vessels (tanks, drums, etc.) that contain chlorinated solvents to minimize release of solvent vapors into the workplace. Most facilities that use chlorinated solvents 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 absorption is the traditional method to capture solvent vapors. The exhaust gasses are passed through a bed of activated carbon, which absorbs the solvent vapors. Studies show that polymeric beds are also very effective at this.

Desorption and recovery processes are critical parts of the overall process. The traditional use of steam to recover solvents from carbon can strip stabilizers from the solvent and generate a considerable amount of water that needs to be treated or decontaminated.

## **Environmental Emission Control - Continued**

Alternative processes use heat and condensation to recover the solvent, with less stabilizer loss and no additional waste stream to treat.

## Prevent and Reduce Water and Soil Contamination

Chlorinated solvents are not "readily biodegradable," according to the definition by the Organization for Economic Cooperation and Development (OECD). While methylene chloride is biodegradable under both aerobic and anaerobic conditions, perchloroethylene biodegrades very slowly. Thus, contamination of groundwater and soil by chlorinated solvents can be a serious problem.

Chlorinated solvents are not very soluble in water, but they can still cause contamination of surface or groundwater. Additionally, because chlorinated solvents are 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 chlorinated solvents will contain some chlorinated solvent, 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. Contaminated soil and water are 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.** 

### 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 chlorinated solvents 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 assumed to be empty.
- Overfilling storage containers and not containing 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.
- Carrying chlorinated solvents in open containers, and disregarding minor spills.
- Carelessness when storing or handling wastes contaminated with chlorinated solvents.
- Not immediately cleaning up leaks and spills when they occur.

## Storage and Equipment



This section provides important information on proper storage guidelines for chlorinated solvents. Specific recommendations are presented for:

- Drum storage
- Bulk storage
- · Tank specifications
- · Underground storage
- · Tank cleaning, repair, and maintenance
- · Solvent sampling
- · Secondary containment
- · Storage of spent solvents
- · Location of pipes, elbows, and fittings
- · Related equipment

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 guidelines for working with chlorinated solvents.

### **Drum Storage**

Chlorinated solvents are often delivered in drums. On arrival, store these drums 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. There are specific national and local regulations governing the use of solvent-resistant materials and solvent-tight containers for storage facilities. You should review and follow all applicable laws and regulations. Never use regular concrete alone when constructing drum storage areas, because chlorinated solvents can permeate concrete. Instead, painted steel is recommended to allow observers to verify the integrity of the storage area. Vacuum concrete is another option to prevent permeation in case of spills.

Drums containing chlorinated solvents should be stored upright. However, you may place drums fitted with a bung valve in a horizontal drum cradle to allow easy transfer of solvents to smaller containers.

Treat any liquid found in retention basins as contaminated solvent waste, unless it is proven to be solvent-free.

### **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 (see Figure 2). A reaction between these metals and the solvent may cause corrosion, and could ultimately cause equipment failure (see Related Equipment, page 20).

## Storage and Equipment - Continued

Figure 2: Bulk Storage Arrangement for Transferring Solvent by Pump Shown: Horizontal Tank With Bottom Connections†



### Legend

- 1) Storage Tank
- (2) Pressure/Vacuum Relief Valve (set @ 75% of tank's rating)
- (3) Manhole (24-inch minimum ID)
- (4) Solvent Temperature Indicator
- (5) Liquid Level Indicator
- (6) Vent Dryer With Dessicant (must be accessible)
- (7) Electrical Grounding
- (8) Vapor Return Line from Bulk Delivery and/or Process
- (9) 2-Inch Schedule 40 Steel Piping
- 10 2-Inch Block Valves
- (1) Product Withdrawal Nozzle (extends up into tank)
- 2 Tank Drain Nozzle (at bottom of tank)
- (3) Strainer (to protect pump and storage tank)

- (A) Centrifugal or Positive Displacement Pump (25-50 gallons per minute)
- (5) Continuous-Pour Concrete Floor
- (6) Secondary Containment (110% of tank volume)
- Dry Break Fittings (2-inch)
- (B) Pump Discharge Pressure Indicator



## Storage and Equipment - Continued

## **Tank Specifications**

Tank specifications should be in accordance with all applicable laws and regulations. The chlorinated solvents discussed in this manual have 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 inprocess filling operations.
- Ensure tanks are grounded to prevent the build-up of static electricity.
- If the tank is located in a containment area, you should follow the applicable laws and regulations for solvent-resistant materials and solvent-tight containers. See Drum Storage (page 17) for more information.

## **Underground Storage**

Locating single-walled storage tanks without adequate leakage control systems underground is **not recommended**, and may be specifically prohibited in some areas. The escape of chlorinated solvents through unobserved leaks may pollute soil and groundwater, and may lead to high costs for removing contaminated wastes.

If underground storage is already in place, install a tank testing and monitoring system, and inspect it regularly.

## Tank Cleaning, Repair, and Maintenance

When getting in contact with chlorinated solvents always ensure that you wear the appropriate personal protective equipment, as a minimum, protective clothing chemically resistant to this material, gloves, and safety glasses. For details see section Personal Protective Equipment, page 11.

Practice continuous maintenance on your tanks to prevent loss of solvent.

Tank cleaning should be directed by thoroughly trained personnel who are familiar with the hazards, appropriate safety precautions, equipment, and first aid guidelines applicable to working with chlorinated solvents.

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<sup>®</sup> 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 guidelines when sampling chlorinated solvents:

- Dry bottles before taking samples.
- Sample bottles should be made of narrow-mouthed glass (preferably amber-colored), with a maximum fill just below 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<sup>®</sup> 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 to take them 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.

## Secondary Containment

To help prevent soil and groundwater contamination, a secondary containment system is strongly recommended, and is a legal requirement in many countries. 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 the 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 demands the same precautions as the storage of fresh solvents. It is very important that spent solvents and solvent-laden waste materials are not put in hermetically sealed containers due to the risk of pressure building from potential uncontrolled reactions, such as the reaction of small particles of metal with chlorinated solvents after inhibitors have been depleted.

## Storage and Equipment - Continued

## Location of Pipes, Elbows, and Fittings

Do not bury pipelines, elbows, and fittings. The pipelines should be readily accessible for frequent inspection, and for immediate detection and repair of leaks. Piping may also be placed in an appropriately sized and solvent-resistant trough to collect any leaking solvent. If buried pipes are unavoidable, they must be jacketed, and a leakage alarm system must be provided for the void between the jacket and the pipe.

## **Related Equipment**

### Pipes

Pipes may be made of carbon steel or stainless steel. To prevent joint failure and the release of solvent, be sure that all piping connections are made with solvent-resistant materials. Recommended pipe connections are first welded, then flanged, and lastly screwed to ensure a leak-free system. Slip-on sockets and soldered connections are not acceptable for service with chlorinated solvents.

Schedule 40 carbon steel pipe is usually sufficient, unless purity requires stainless steel. If you must use screwed fittings, wrap the threads of the fittings with tape made from polytetrafluoroethylene (PTFE) or Teflon<sup>®</sup> to prevent leaks. Do not use "pipe dope." Remove cutting oils and other dirt before placing the pipe in service. Pipe sections that can be closed off by valves should be protected with relief valves if pressures can exceed the burst pressure of the pipe.

#### **Unloading Hose**

A two-inch-diameter, seamless, flexible metal hose, preferably stainless steel, can be used to unload tank cars. PTFE-lined hose sheathed in a metal braid (such as stainless steel or bronze) or in neoprene rubber is also satisfactory. Interlocked, spiral-type hose should never be used, as it will allow solvent to leak through the packing. Order hose in the required length, with fittings already installed by the manufacturer.

Use of dedicated transfer hoses for each solvent is preferred over commonuse unloading hoses found on transport equipment or unloading stations. Develop hose-inspection and pressure-testing programs to ensure that the integrity of hoses is maintained and that replacement occurs when needed.

### Pumps

When selecting a pump, it is important to consider the high vapor pressure of the product when the lifting capability of the pump is calculated. This is especially true for methylene chloride. Centrifugal pumps or positive displacement pumps of ductile iron or carbon steel casing are satisfactory for transferring chlorinated solvents. Pumps should be equipped with a stainless steel shaft and double mechanical seals. Cast iron is not recommended for pumps.\*\*

#### Valves

Steel ball, gate, or globe valves are satisfactory. Ball valves should have a PTFE seat, and globe valves should have a metal seat. Rings of PTFE or flexible graphite may be used as stem packing. Where full-line flow is desired, ball or gate valves are recommended. Where throttling is necessary, globe or needle valves may be used. Swing and lift valves are both satisfactory as backflow prevention (check) valves. Cast iron is not recommended for valves.\*\*

\*\*Cast iron is not recommended. Cast iron pumps or valves are susceptible to breaking or cracking due to mechanical strain and temperature changes. This may lead to leaking of the chlorinated solvents.

### Seals and Gaskets

These materials must be solvent-resistant, flexible enough to conform to the flange, and resilient enough to recover from compression. Impregnated cellulose fiber, cork-base materials, and PTFE-impregnated graphite are representative materials. VITON<sup>™</sup> resin is acceptable, except for use with methylene chloride, since the VITON<sup>™</sup> will swell in liquid contact with the solvent. Teflon<sup>™</sup> is recommended for use with methylene chloride. Gaskets of rubber or synthetic rubber, such as neoprene rubber or BUNA-N, should not be used with any of the chlorinated solvents.

#### Meters

Meters for measuring flow, pressure, and/or temperature should be suitable for use with the particular solvent you are handling. Obtain information on suitability directly from the manufacturer. Meters should not have any aluminum, magnesium, or zinc components, or any alloys of these materials.

### **Additional Information**

The European Chlorinated Solvent Association (ECSA) provides more information about the selection of pumps, gaskets, valves, and piping that are intended for use with chlorinated solvents.

For a copy of Storage and Handling Chlorinated Solvents, you can download the PDF at <u>www.chlorinated-solvents.eu</u> or send your request to ecsa@cefic.be.

## Unloading and (Re)Packaging



This section presents important information on proper handling guidelines for chlorinated solvents. Specific recommendations are presented for unloading bulk solvent. 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 guidelines for working with chlorinated solvents.

## **Unloading Bulk Solvent**

Properly trained and equipped personnel, who are present at all times, should carry out unloading operations in areas that are contained with a solvent-resistant material. Whenever a container is unloaded by gravity or a 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 percent 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:

- Verify that the receiving tank is correct, and ensure it 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 (see Solvent Sampling, page 19).
- 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.

Customers who receive bulk quantities of chlorinated solvents 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. To provide adequate ventilation and to prevent spills and solvent contamination, make sure that all fittings and transfer operations take place in an area protected with safety and environmental controls.

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 the drumming station. Provide secondary containment for both the truck and the drumming station, and follow all other general unloading procedures (see Figure 3, page 22).

### Transfer from Storage to Point of Use

The simplest and most economical method of transfer is to pipe the solvent directly to the point of use, using gravity flow. If the point of use is far away, or higher than the storage tank, then use an appropriate pump with permanently installed pipe.

When delivering solvent to the bottom of a receiving vessel, make sure it is at a point below the fluid surface to minimize turbulence and unnecessary evaporation. Regularly inspect and properly maintain all piping, valves, and pumps.

Do not transfer even small amounts of chlorinated solvent in open containers. If permanently installed piping is not available, use a mobile tank with covered openings and pressure relief to move the solvent to the application that needs filling. Always use proper nozzles and approved fluid flow lines to connect the mobile tank to the machine. Vapor return lines from the point of use back to the storage tank will minimize solvent vapor emissions during transfer.

### 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 should be visible. If the containers will be exported, the language on the label should be understandable by the receiving party. You must always label containers in accordance with applicable laws and regulations for the countries in which you are operating.

## Unloading and (Re)Packaging - Continued

Figure 3: Semiautomatic Drumming Station Using a Scale for Drumming Solvents From Tank Trucks



#### Legend

- 1) Static Electricity Ground
- ② Clamps and Ground Wires for Piping, Pumping and Filling System
- ③ Customer's Manual Valve—Note: Do not open until pipe connections and filling equipment have been checked.
- Truck Valve and Operator
- ⑤ Posted Operation Instructions
- (6) Pump Switches Controlling Centrifugal Pump and Fan Switch
- ⑦ Filling Station—Dial Scale with Automatic Shutoff, Filling Drums Using a Bottom-Filling Drum Lance (Max. Cap. 60 GPM)
- (8) Exhaust Fan-Pickup at Drum Bunghole and Floor Level

<sup>2</sup> Drainings must be collected from the line drain.

- (9) Eye Wash/Safety Shower Station(s)
- Image Energency Stops—Locations at Pump, Filling Station, and Others If Required
- I Fire Blanket/Protective Equipment Cabinet
- (2) Spill/Leak Drainage to Sump1
- 3 Wheel Chocks
- (14) Vent Scrubber
- (5) Pressure Switch—Shuts Off Pump When Valve Closes
- Operator Emergency Escape Routes
  - 7 Sample Valve
  - (B) Line Drain / Cleanout Connection<sup>2</sup>

The sump should be contained, not drained into the sewer.

## Accidental Release/Disposal



## Handling

Those responsible for handling, treating, storing, and disposing of chlorinated solvents and solvent wastes must understand and follow approved guidelines and relevant government regulations for the handling, treatment, storage, and disposal of chlorinated solvents and their waste. Laws dictating how a user may handle, treat, store, and dispose of hazardous waste vary. Olin recommends that you contact a licensed disposal contractor to handle any waste or contaminated material where this is to be sent off-site. If you intend to treat any contaminated material on-site, Olin recommends that you contact a qualified environmental engineering company to assist with the permitting and design of any such treatment system and contact the local environmental regulator with respect to any permits or licenses that may be required.

## What to Do When Spills or Leaks Occur

Spilled solvent and solvent-contaminated water should never be allowed to drain off into sewers or any body of water, or onto the ground. It is important to inspect and maintain your process equipment, holding tanks, and spill-control devices continually, and to know what to do ahead of time if a spill or leak occurs. Be prepared by having proper protective equipment identified and available for personnel cleaning up any spills.

If you or a fellow employee experience symptoms of dizziness, loss of coordination, or eye irritation—or if breathing becomes difficult leave the area immediately, and seek fresh air. Call a physician and/ or take the employee to an emergency medical facility. If a colleague stops breathing, remove to fresh air and perform mouth-to-mouth resuscitation and seek medical assistance immediately.

## **Emergency Guidelines for Spills and Leaks**

### Guidelines for Small Spills and Leaks

- 1. Maintain proper protective equipment, and keep it available for personnel cleaning up the spill.
- 2. Contain the spill.
- 3. Stop the leak using proper protective equipment and ventilation.
- 4. Clean up small spills and leaks immediately using mops, rags, cloths, sawdust, or compatible chemical binders (absorbents) such as bentonite or vermiculite.
- 5. Place solvent-laden materials and/or binders in a covered, solvent-resistant metal container.
- 6. Arrange for proper waste disposal according to applicable laws and regulations.
- 7. Contact the supervisor, even for small spills and leaks.

### Guidelines for Large Spills

- 1. Evacuate the area and call for help immediately.
- 2. Ventilate the area.
- 3. Notify the supervisor.
- 4. Protect yourself. Do not approach the spill area without wearing self-contained, positive-pressure respiratory equipment, and suitable protective clothing.
- 5. Contain the spill.
- 6. Block floor drains, if present, to prevent the spill from spreading further.
- 7. Pump spilled solvent into a solvent-resistant container. Close and label the container.

## Accidental Release/Disposal - Continued

- 8. Absorb residual spilled solvent with compatible chemical binders (absorbents) such as bentonite, vermiculite, or sawdust, and then transfer to a closed container for proper disposal.
- 9. Spills may have to be reported to the proper authorities if quantities exceed reportable volumes.

After a spill, if the product is reusable, refer to the Reduce, Reuse, Recycle section below. The preferred method for disposing of chlorinated solvents and the materials used for cleanup is to send the waste, via an authorized waste hauler, to a licensed reclaimer or to a government-approved incinerator. Perform repairs and/or take corrective action to prevent recurrence.

## Reduce, Reuse, Recycle

It is not acceptable to dispose of chlorinated solvent wastes in landfills. Olin encourages users to reduce, reuse, and recycle chlorinated solvents as much as possible in any operation. Many countries have established pollution management standards based on the following principles:

- Reduce the use of chlorinated solvents at the source by choosing process equipment that minimizes fugitive emissions, or use control systems that capture emissions for recovery.
- Reuse/recycle chlorinated solvents by recovering and purifying solvent through filtration and distillation.
- Contact a reputable recycling company in your area to reclaim spent chlorinated solvents.

# Disposal of Spent Solvents, Waste, and Used Drums

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

Never dispose of chlorinated solvent waste by pouring it on the ground, down a sewer, or into a septic system. Do not dispose of chlorinated solvent 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.

Containers must be disposed of in accordance with all applicable federal, state, and local regulations. Offer the empty container to a qualified reconditioner, or crush and dispose of the container in accordance with procedures approved by relevant jurisdictional regulators such as local authorities. All drum labels should be defaced or removed, and all other drum markings are to be removed prior to disposal or transfer to a qualified reconditioner.

Olin does not approve of the reuse of chlorinated solvent drums.

## **Appendix A - Physical and Chemical Properties**

### Table 5: Physical Properties of Chlorinated Solvents

	Solvents	
Properties	Methylene Chloride	Perchloroethylene
Chemical Formula	CH <sub>2</sub> Cl <sub>2</sub>	C <sub>2</sub> Cl <sub>4</sub>
Molecular Weight	84.9	165.8
Boiling Point @ 760 mmHg	103.6°F (39.8°C)	250°F (121°C)
Freezing Point	-142°F (-97°C)	-8°F (-22°C)
Specific Gravity @ 25 °C/25 °C	1.32	1.62
Pounds per Gallon @ 25 °C	10.98	13.47
Vapor Density (air=1.00)	2.93	5.76
Specific Heat @ 25 °C cal/g°C	0.283	0.209
Heat of Vaporization @ Boiling Point cal/g BTU/lb	78.9 142.0	50.1 90.2
Refractive Index @ 25 °C	1.421	1.503
Viscosity @ 25 °C Centipoise	0.41	0.84
Flash Point Tag Open Cup ASTM, Method D-1310 Tag Closed Cup ASTM, Method D-56	None None	None None
Solubility (g/100g) @ 25 °C H₂0 in Solvent Solvent in H₂0	0.17 1.3	0.011 0.015
Surface Tension (dynes/cm @ 25 °C)	27.1	31.8
Kauri Butanol Value	136	90
Solvent-Water Azeotropic Boiling Point	100.6°F (38.1°C)	190°F (87.8°C)
Flammable Limits (Volume% of Solvent in Air) @ 25 °C Lower Limit Upper Limit	14 22	None None
Autoignition Temperature	1033°F (556°C)	Noncombustible
Vapor Pressure @ 20 °C	355 mmHg	14 mmHg
Octenol/Water Partition	1.25	3.4
Kinematic Viscosity @ 25 °C	0.31mm²/s	0.52 cSt

Disclaimer: The data above represents physical properties only, and should not be construed as product specifications.

## **Appendix B - Gloves for Use with Chlorinated Solvents**

The EN 374-2004 Standard specifies the capability of gloves to protect the user against chemicals and/or micro-organisms.

Use chemical resistant gloves classified under EN374: liquid-proof gloves, breakthrough time >30 min. Gloves of this category should carry the pictogram:



The pictogram is accompanied by a 3-digit code indicating the solvents against which it is tested. Letter D indicates resistance against Dichloromethane (Methylene Chloride) and is recommended for contact with chlorinated solvents.

Preferred Glove Material:

- Ethyl vinyl alcohol laminate ("EVAL")
- Polyvinyl alcohol ("PVA")
- Viton<sup>™</sup>

### EN 374 Classification and Breakthrough Times

Breakthrough times are determined against 12 chemicals listed in EN 374, which include Methylene Chloride. Gloves are classified depending on the breakthrough time into 6 different classes.

### Table 6: Classification and Breakthrough Times

Measured Breakthrough Time	Protection Index	Measured Breakthrough Time	Protection Index
> 10 minutes	class 1	> 120 minutes	class 4
> 30 minutes	class 2	> 240 minutes	class 5
> 60 minutes	class 3	> 480 minutes	class 6

Permeation is usually tested at room temperature. A temperature increase of 10 °C generally cuts the breakthrough time in half and doubles the permeation rate (rate of penetration of amount of solvents through the glove layer, measured in mg/sec/m<sup>2</sup>).

When prolonged or frequently repeated contact may occur, a glove with a protection class of 5 or higher (breakthrough time greater than 240 minutes according to EN 374) is recommended. When only brief contact is expected, a glove with a protection class of 3 or less is recommended.

Glove thickness alone is not a good indicator of the level of protection a glove provides against a chemical substance. This mainly depends on the specific composition of the material from which the glove is fabricated.

The thickness of the glove must, depending on model and type of material, generally be more than 0.35 mm to offer sufficient protection for prolonged and frequent contact with the solvent.

As an exception to this general rule, it is known that multilayer laminate gloves may offer prolonged protection at thicknesses less than 0.35 mm. Other glove materials with a thickness of less than 0.35 mm may offer sufficient protection when only brief contact is expected.

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 like other chemicals which may be handled, physical requirements (cut/puncture protection, dexterity, thermal protection), potential physiological reactions to glove materials, as well as the instructions/ specifications provided by the glove supplier.

## Appendix C - Property vs. Temperature Graphs

### Table 7: Relative Evaporation Rates\*

n-Butyl acetate1.0	Trichloroethylene3.0
Ethanol‡1.4	Methyl ethyl ketone
Perchloroethylene1.5	Acetone5.7
Methyl alcohol2.1	Methylene chloride7.0

\*Evaporation rates measured with respect to n-butyl acetate. Larger numbers reflect faster evaporation. As measured by ASTM D3539-76. \*95% Et OH, 5% H,0

### Figure 4: Vapor Pressure of Chlorinated Solvents



## Figure 5: Density of Chlorinated Solvents as a Function of Temperature





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