Chlorinated Solvents—Still the Best Choice for Vapor Degreasing

By James A. Mertens

A misunderstanding has been making the rounds among manufacturers involved in surface cleaning: The belief that chlorinated solvents are on the way out. The reverse is the case. Chlorinated solvents are still very viable products, and remain one of the best choices for surface cleaning and vapor degreasing. The dilemma concerning how to meet exposure limits when degreasing with chlorinated solvents is discussed here.

A major contributor to the misunderstanding surrounding this issue has been the banning of 1,1,1-trichloroethane—at one time the most popular of the chlorinated solvents. This solvent was phased out of production as a depleter of stratospheric ozone under the provisions of the U.S. Clean Air Act (CAA) and the international Montreal Protocol.

Problems related to one member of the chlorinated solvents family, however, should not reflect on the other members. The fact is that the other chlorinated solvents—methylene chloride (MEC), perchloroethylene (PCE) and trichloroethylene (TCE), have no effect on stratospheric ozone and, therefore, are not regulated for ozone-depleting potential (ODP). In fact, these three solvents have been approved as replacements for 1,1,1-trichloroethane under the U.S. Environmental Protection Agency's (EPA's) Significant New Alternatives Policy (SNAP) ruling.

In spite of the vast array of surface cleaning products and processes—including aqueous, semi-aqueous, hydrocarbon and mechanical cleaning methods—many manufacturers who experimented with alternatives to 1,1,1-trichloroethane have returned to chlorinated solvents. Their reasons involve the advantages that these solvents offer, advantages that are difficult to duplicate among the alternatives. Chlorinated solvents have excellent solvency, are virtually nonflammable,* and have low toxicity when used in accordance with established safety procedures. In addition, they are:

- The lowest-cost, nonflammable solvents on the market.
- Of all solvents, the ones most thoroughly studied from both health and environmental standpoints.
- Characterized by a long historical track record with many manufacturers.
- Noncorrosive to most metal substrates subject to surface cleaning, and to most metals used in cleaning equipment.
- Easily recycled for continuous cleaning.

Also, the chlorinated solvents can be used with a variety of equipment upgrades and new equipment designs that control emissions and make it possible to meet the exposure levels required by the strictest regulations.

The Three Chlorinated Solvents

Each of the three chlorinated solvents has its own advantages for specific applications, based on its physical profile:

Methylene Chloride

Methylene chloride (MEC, also called dichloromethane) is a powerful and versatile chlorinated solvent known for its high solvency capabilities. MEC has the lowest boiling point—103.5 °F (39.7 °C)—and lightest vapor density—2.93 times that of air—of the chlorinated solvents. It is a clear, heavy liquid (10.98 lb/gal), and it freezes at -139 °F (-95 °C).

Because of its low boiling point, MEC is often used for degreasing sensitive parts, such as thermal switches and thermometers, which would be damaged by high temperatures. It is also chosen when parts must be near room temperature after cleaning for immediate handling, or for tolerance testing and measurements.

Perchloroethylene

Perchloroethylene (PCE or perc, also called tetrachloroethylene) is a clear, colorless liquid with a distinctive, somewhat ether-like odor. It has the highest boiling point (250 °F or 121.1 °C) and freezing point (-9 °F or -22.8 °C), weight (13.47 lb/gal) and vapor density—5.76 times that of air—of the chlorinated solvents.

The high boiling point of PCE makes it especially effective in removing high-melting pitches and waxes, and for cleaning grossly contaminated parts. The high temperature of PCE vapors also permits complete and thorough drying of work by vaporizing moisture entrapped in porous metals, deeply recessed parts and blind holes.

Trichloroethylene

Trichloroethylene (TCE) is a clear, heavy liquid—12.11 lb/gal—with excellent solvency. Long-recognized for its cleaning power, TCE boils at 189 °F (87 °C) and freezes at -124 °F (-86.7 °C). The high density of TCE's vapor—4.53 times that of air—assures low vapor loss and easy recovery from vapor degreasing systems.

TCE's aggressive solvent action works well on the oils, greases, waxes, tars, lubricants and coolants generally found in the metal processing industries. It is especially effective in removing difficult soils, such as semi-cured varnish or paint films, heavy rosins and buffing compounds.

These three solvents are widely used in surface cleaning, particularly in the vapor degreasing process, in which the work to be cleaned is exposed to vapors from heated solvents. These vapors condense on the work, dissolving oils and greases and carrying off soils and fines.

The chlorinated solvents are also used in cold cleaning, both dip and wipe methods, but the need to keep workplace vapor levels and environmental vapor losses low, in accordance with federal, state and local regulations, limits their use in cold processes.

** See the respective Material Safety Data Sheet (MSDS).*

Regulatory Overview

When the U.S. EPA published its SNAP ruling for ozone-depleting substances in March 1994, it gave industry the official go-ahead to consider the three chlorinated solvents as acceptable alternatives to 1,1,1-trichloroethane. Published on March 18, 1994, in the *Federal Register* (59 FR 13044-13161), this rule applies to surface cleaning, as well as other applications.

This policy also pointed out that worker exposure and environmental emissions of these solvents should be controlled properly and in accordance with other environmental, workplace and consumer regulations established by EPA and other agencies.

In light of EPA's statements in the SNAP rule, some manufacturers, such as The Dow Chemical Company, support the use of MEC, PCE and TCE in cases where nonflammability is a critical prerequisite for safety, and where personal health hazards and environmental contamination are reduced to a minimum by engineering and operating design.

The three chlorinated solvents are subject to other federal regulations, including those governing hazardous air pollutants, as well as the Clean Water Act (CWA), the Occupational Safety & Health Administration (OSHA), Resource Conservation & Recovery Act (RCRA) and Comprehensive Environmental Response, Compensation & Liability Act (CERCLA). In addition, TCE is regulated under rules governing volatile organic compounds (VOCs), although both MEC and PCE are exempt from VOC regulations. Clear and precise directions, processes and services are available from government agencies, trade associations and solvent suppliers to help users of chlorinated solvents comply with all the regulations.

A brief summary of federal regulations applying to the chlorinated solvents is given in Table 1.

Vapor Degreasing—The Traditional Method

Traditionally, the vapor degreasing process is carried out in either a batch or an in-line degreaser. The standard batch degreaser is an open-top tank into which the dirty parts are lowered. Solvent in the bottom of the tank is heated to produce vapor, and because the vapor is heavier than air, it remains in the tank. Cooling coils below the lip of the tank create a cool zone, which forms the upper boundary of the vapor zone.

The degreasing process may be supplemented by adding a spray lance to the open-top degreaser, so that hard-to-remove soils can be flushed off by the operator. In addition, many degreasers also contain one or several immersion tanks below the vapor zone so that parts can be lowered into liquid solvent—often in a tumbling basket—before being raised into the vapor for final rinsing.

If scrubbing is required to remove heavy oil deposits and solids, ultrasonic cleaning can be added by installing transducers in the degreaser. When ultrasonic energy is transmitted to a solution, it produces cavitation—the rapid buildup and collapse of thousands of tiny bubbles, which impart a scrubbing action to the surface of soiled parts.

Although the vapor generally stays below the cool zone of an open-top degreaser, there is always some solvent loss. Drafts in the area around the degreaser will cause solvent vapor to be pulled out. Parts-loading causes losses as work to be cleaned disturbs the solvent/air interface. In addition, cleaned parts may also carry solvent with them when removed from the degreaser. Up to 70 percent of the solvent in a traditional open-top degreaser can be lost through these factors over the course of a year.

Enclosed Vapor Degreasing

In-line vapor degreasers include several types of conveyorized equipment—large, automatic units that can handle a large volume of work and are enclosed to provide minimal solvent loss. These units include the monorail, cross-rod and vibratory degreasers.

The monorail conveyorized degreaser uses a straight-line conveyor to carry parts into the degreaser, lower them into the vapor zone, raise them into a cooling zone and, finally, out of the degreaser. This process is ideal when production rates are high and large parts to be cleaned can be suspended from hooks or hangers.

The cross-rod conveyorized degreaser is generally used for processing small parts in baskets, trays or even mesh cylinders. In this equipment, the parts are placed in the degreaser and removed from it at the same opening, while the conveyor carries the work through immersion dips, vapor zones and drying zones.

The vibratory degreaser is a patented unit. In this process, the work is dipped in solvent, then rises on a vibrating spiral elevator trough through a counter-flowing rinse of clean solvent distillate, a vapor zone and, finally, a drying section.

Although these units are enclosed, there is still some solvent loss through the openings where work enters and leaves the equipment, and through the joints and seams of the equipment. Consequently, procedures are called for to minimize this loss, in order to provide a working environment in which vapor exposure is below the levels permitted by OSHA regulations, and an industrial environment that meets requirements set by the EPA.

Emission standards for chlorinated solvent degreasing operations are now governed by EPA's National Emission Standards for Hazardous Air Pollutants (NESHAP) for new and existing halogenated solvent cleaning operations. These standards cover both vapor degreasing and cold cleaning with methylene chloride, perchloroethylene and trichloroethylene, as well as chloroform. The goal of the NESHAP regulation is an overall reduction in solvent emissions of 50–70 percent of current nationwide emissions.

Technology Meets the Needs

The NESHAP provides a number of control procedures for reducing solvent emissions from equipment. Operators of batch vapor degreasers and in-line cleaning machines may choose from a series of combinations of two or three of the procedures, which include:

- Freeboard ratio of 1.0—The height of the freeboard above-vapor level must be equal to the width (shorter dimension) of the degreaser.
- Freeboard refrigeration device—This is a refrigerated system that supplements or replaces the traditional water cooling system and creates a cold-air blanket above the vapor zone.
- Reduced room draft—Wind speed above the freeboard must not

Table 1
Chlorinated Solvents Regulatory Summary

Regulation	Trichloroethylene	Perchloroethylene	Methylene chloride	1,1,1, Trichloroethane*
Ozone depletion (CAAA, Montreal Protocol)	No	No	No	Yes
VOC state-to-state differences	Yes <100 tpy marginal[1] <50 tpy serious <25 tpy severe <10 tpy extreme	No[2]	No[3]	No[4]
Permits CAA Title V	Yes 10 tpy or combination of 25 tons HAP	Yes 10 tpy or combination of 25 tons HAP	Yes 10 tpy or combination of 25 tons HAP	Yes 10 tpy or combination of 25 tons HAP
HAP NESHAP	Yes	Yes	Yes	Yes
Clean Water Act	Yes	Yes	Yes	Yes
OSHA	Yes	Yes	Yes	Yes
PEL	50 ppm[5] Worker right to know; training; recordkeeping; reporting	25 ppm[6] Worker right to know; training; recordkeeping; reporting	25 ppm[7] Worker right to know; training; recordkeeping; reporting	350 ppm Worker right to know; training; recordkeeping; reporting
RCRA	Yes <100 kg: Cond. exempt small quantity generator 100-1000 kg: Small quantity generator >1000 kg: Large quantity generator	Yes <100 kg: Cond. exempt small quantity generator 100-1000 kg: Small quantity generator >1000 kg: Large quantity generator	Yes <100 kg: Cond. exempt small quantity generator 100-1000 kg: Small quantity generator >1000 kg: Large quantity generator	Yes <100 kg: Cond. exempt small quantity generator 100-1000 kg: Small quantity generator >1000 kg: Large quantity generator
CERCLA (Superfund reportable quantities)	Yes 100 lb reportable quantity spill	Yes 100 lb reportable quantity spill	Yes 1000 lb reportable quantity spill	Yes 1000 lb reportable quantity spill

*1,1,1-Trichloroethane included for comparison.

[1] In areas of the country classed as having a marginal smog problem up to 100 tpy emissions are allowed to a facility. Allowable emissions are lower in areas with more serious problems.
[2] Perchloroethylene listed as exempt February 7, 1996 *Federal Register*, 4588.
[3] Methylene chloride listed as exempt July 8, 1977, *Federal Register*, 35314.
[4] 1,1,1-trichloroethane listed as exempt July 8, 1977, *Federal Register*, 35314.
[5] This limit in OSHA's 1989 rule has been overturned. Dow continues to use these 1989 PELs in MSDS and labels.
[6] This limit in OSHA's 1989 rule has been overturned. Dow continues to use these 1989 PELs in MSDS and labels.
[7] Currently challenged by industry. ACGIH recommends 50 ppm, and Dow supports this limit.

exceed 50 ft/min (15.2 meters/min).

- Working-mode cover—This is defined as any cover or machine design that shields the cleaning machine from outside air disturbances during the parts-cleaning cycle.
- Dwell—This refers to the time in which cleaned parts remain in the freeboard area above the vapor zone after cleaning. EPA defines proper dwell time as 35 percent of the time required for the parts to cease dripping in the vapor zone.
- Superheated vapor (vapor temperature maintained 10 °F above the boiling temperature of the solvent)—This promotes more thorough drying of the work before it is removed from the degreaser.
- Carbon adsorption equipment in the ventilation system connected with the degreaser.

In addition, vapor degreasing operators must employ an automated hoist or conveyor that carries parts at a controlled speed of 11 ft/min or less, through the complete cleaning cycle.

It has been found that each of these procedures, used alone, will reduce solvent loss by a respectable amount, while combining two or three procedures reduces loss even further. Creating a freeboard ratio of 1.0 in an open-top degreaser, for example, will reduce loss by 30–40 percent over the traditional process. Combining an increased freeboard ratio with superheated vapor or reduced room draft increases the control level to 60 percent. In most cases, in fact, if a user combines three of the procedures, the control can be brought up to 70 percent. Table 2 illustrates how these incremental improvements can be brought about.

These technical options have been incorporated into many of the degreasers currently on the market. In some cases, it may be more cost-effective to invest in new equipment of this type than to upgrade the existing equipment.

Table 2
Incremental Value of Upgrades*

NESHAP Option or Control Combination	Primary Control Option	Secondary Control Option	Tertiary Control Option
1	Freeboard Ratio = 1 30%	Superheated Vapor +30%	Automatic Cover +10% = 70%
2	Freeboard Refrigeration 30%	Superheated Vapor +30% = 60%	
3	Freeboard Refrigeration 30%	Automatic Cover +20% = 50%	
4	Freeboard Ratio = 1 30%	Superheated Vapor +30%	Reduced Room Draft +10% = 70%
5	Freeboard Refrigeration 30%	Reduced Room Draft +20% = 50%	
6	Freeboard Refrigeration 30%	Freeboard Ratio = 1 +30% = 60%	
7	Freeboard Refrigeration 30%	Dwell Time +20% = 50%	
8	Freeboard Ratio = 1 40%	Reduced Room Draft +20%	Dwell Time +10% = 70%
9	Freeboard Refrigeration 30%	Carbon Adsorption +30% = 60%	
10	Freeboard Ratio = 1 30%	Superheated Vapor +30%	Carbon Adsorption +10% = 70%

*All values are approximate, compiled from tests at a number of companies.

"Emissionless" Vapor Degreasing

Many companies have found it cost effective to adopt one of the new degreasers that has no air/vapor interface. These sealed and virtually emissionless units were first introduced in Europe to meet health and environmental regulations, which are considerably more stringent than U.S. regulations.

Typically, these degreasers perform the cleaning operation in a sealed chamber into which solvent is introduced *after* the chamber is closed. Solvent vapor is introduced as the final rinse, and all vapors are exhausted after each cycle and passed into a solvent recovery system. With the sealed chamber, control of solvent loss exceeds 90 percent—in other words, virtually no solvent escapes.

Programmed automated operation permits a variety of cleaning programs, including cold or warm solvent-dipping, as well as vapor degreasing. Solvent recovery cycles make use of advanced methods of carbon adsorption and hot-air desorption.

The manufacturer of one such unit, a "closed open-top degreaser" with a large cleaning chamber, claims that solvent emission losses average less than 100 lb/yr. Solvent concentrations in the work area of the closed open-top unit average between 5–10 parts per million (ppm), well below the permissible exposure limits set by OSHA for the chlorinated solvents.

Although these "emissionless" units are costly, a number of plants in the U.S. have found them economical, because they:

- Provide excellent compliance with safety and environmental regulations,
- Conserve solvent,
- Save floor space and
- Provide excellent parts-cleaning performance.

Several brands of these "emissionless" degreasers are currently available in the U.S.

Another European development that is making its debut in North America is emission-free solvent delivery. A line of safety container systems[a] that was originally developed in Europe consists of a closed-loop system that transfers solvent from an enclosed container to the customer's degreasing unit or storage tank, and also transfers waste solvent from the customer's tank to another enclosed container for recycling or disposal. The transfer system is able to pass solvent in one direction, and return solvent vapor in the other, through dry-disconnect fittings that prevent the loss of either solvent or vapor. Dow's system has already undergone testing in the U.S., and is being implemented in some markets.

Supporting Your Solvent Use

Most producers and distributors of chlorinated solvents provide support for solvent users. The Responsible Care® initiative of the Chemical Manufacturers Association, to which all solvent producers subscribe, and the Responsible Distribution Code of the National Association of Chemical Distributors require members to share product stewardship information, safety training and regulatory data with customers. When selecting a supplier, be sure to review what kind of support is provided.

Here, for example, is a brief overview of the support provided by Dow:

- Safety literature—In addition to the MSDS, a product stewardship manual is provided, detailing safe handling and disposal procedures, an illustrated safety brochure for

®Registered service mark of the Chemical Manufacturers Association.
[a] Safety Container, Safechem Umwelt Service GmbH, Dusseldorf, Germany (currently being introduced in the U.S. by The Dow Chemical Company).
[b] MAXISTAB stabilizers, trademark of The Dow Chemical Company.

operating personnel (in both English and Spanish), a safety wall poster with pictograms to aid comprehension (also in both English and Spanish) and a bi-monthly newsletter with information on regulations, as well as on safe and responsible solvent handling.

- Training program—Company personnel hold seminars for solvent users and operating personnel at customer plants and central locations, where several customers can meet, and provide training tapes for customers to show to employees.
- Solvent vapor monitoring—A program to distribute vapor monitoring badges for operating personnel, and to analyze the badges helps solvent users determine whether they are operating within parameters set by regulations.
- Solvent testing—To make sure the solvents remain effective, test kits are available to detect warning signs of solvent degradation. The traditional acid acceptance test is still an important part of the solvent maintenance program. The lower emission systems, however, have shown that additional monitoring and maintenance is required. Dow has developed a new reserve alkalinity test and the associated testing procedures to monitor the more sensitive stabilizer changes that might occur in the system. To complement the solvent testing procedures and enhance the solvent performance, proprietary stabilizers[b] have been introduced.
- Technical assistance—Two telephone numbers are provided to customers: One for emergency assistance and one for non-emergency technical questions. In addition, a technical staff provides on-site auditing and help to customers with special needs.

Still the Best Choice

Today, more and more manufacturers are agreeing that the chlorinated solvents are still the best choice for their surface cleaning processes. Despite the phaseout of 1,1,1-trichloroethane, the other chlorinated solvents—methylene chloride, perchloroethylene and trichloroethylene—remain the most effective and economical surface cleaning agents on the market today.

There are many advantages to the chlorinated solvents: High solvency, high performance, nonflammability, easy to recycle and good economics. Added to this is the long historical use in surface cleaning applications, with well-known safety procedures and voluminous health and epidemiological studies. These make the chlorinated solvents a known quantity to industrial hygienists.

Finally, the development of new, low-emission degreasing equipment and the practice of retrofitting existing equipment to improve performance, result in an impressive environmental record for today's solvent users. All told, the chlorinated solvents remain an important part of the manufacturing process. P&SF

About the Author

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