Replacing 1,1,1-Trichloroethane With Other Chlorinated Solvents

By Vicki L. Rupp & Janet C. Hickman

Cleaning and degreasing metal parts before plating or coating is an important step in the manufacturing process. For a large percentage of companies, and for a long time, this has meant vapor degreasing with 1,1,1-trichloroethane (TCA, also known as methyl chloroform or MCF). Times are changing, however. Production of TCA for emissive applications, such as degreasing, ceases in all developed countries as of the last day of 1995, leaving many manufacturers in a quandary. Until recently, the Dow Chemical Company, Midland, MI, was the only U.S. chemical producer to manufacture a complete line of chlorinated solvents, including TCA and carbon tetrachloride, which have been implicated in the depletion of the stratospheric ozone layer. As of April 1994, the company discontinued the production of TCA. Dow and other suppliers continue to actively pursue answers to the solvent alternatives problem.

Although recycled TCA and TCA from inventories will still be available after January 1, 1996—and although manufacturers in developing countries are permitted an extension of several years on the phaseout—the great majority of users are actively seeking a replacement for the solvent. Fortunately, the Significant New Alternatives Program (SNAP), published by the U.S. Environmental Protection Agency (EPA) in March 1994, has brought a long-needed solution to the problem: Maintain the vapor degreasing process while replacing TCA with one of the other chlorinated solvents.

TCA—Formerly The Solvent of Choice

The benefits of degreasing with TCA are well known. Parts leave the degreaser dry and ready for the next production stage. The process is cost-effective and energy-efficient, and has a small floor-space requirement. In addition, the solvent has excellent cleaning capacity for greases and oils, and is not likely to cause rust damage. It has low toxicity, a high permissible exposure level (PEL), is not flammable under most conditions, and is listed as a non-volatile organic compound (VOC). Consequently, for a number of years TCA had virtually replaced most other solvents for the vapor degreasing process, as well as for cold cleaning and electronic cleaning.

Under the U.S. Clean Air Act Amendments of 1990, however, as well as the international Montreal Protocol, TCA was classified as an ozone-depleting substance (ODS) and is scheduled for production phaseout for all emissive applications by December 31, 1995. In view of this requirement, many users of the solvent have been converting to substitutes or alternatives.

The Search for Alternatives

Unfortunately, good alternatives are hard to find. Those based on a different, non-chlorinated chemistry often require considerable testing, plus costly re-engineering. Although there are no exact "drop-in replacements," the closest alternatives are the other three readily available chlorinated solvents—methylene chloride (MEC), perchloroethylene (perc or PCE) and trichloroethylene (TCE).

These three solvents share most of the advantages of TCA, such as:

- Excellent solvency
- Virtually non-flammable
- Low toxicity when used in accordance with established safety procedures.

In addition, these solvents have not been implicated as sources of stratospheric ozone depletion, are not scheduled for phaseout, and are not subject to the excise taxes levied on ODSs. Despite their similarity to TCA, these alternate solvents also have certain characteristics of their own that make them particularly suitable for specific types of degreasing.

Methylene Chloride (MEC)

MEC (also called dichloromethane and methylene dichloride) is a powerful and versatile chlorinated solvent known for its high solvency capabilities. It has a mild ethereal odor and is completely miscible with a variety of solvents.

A clear, heavy liquid (10.98 lb/gal), MEC has the lowest boiling point (103.5 °F; 39.8 °C), the lightest vapor density (2.93 times that of air), and the highest solvent power of the chlorinated alternatives. It freezes at -139 °F (-95 °C).

With its low boiling point and high solvent power, MEC is well suited for cleaning temperature-sensitive parts, such as thermal switches and thermometers, and for removing tough paint residues, hard-to-dissolve resins, and gross metal fines. It can be also used effectively on white metals (aluminum and zinc). In vapor degreasing, its low boiling point and ability to dry quickly have permitted high throughput at an acceptable cost.

On the other hand, the high solvency of MEC may be too aggressive for some substrates, such as plastics and rubber. Further, because it passes rapidly into the vapor phase, it is difficult to contain the vapor. When converting a degreasing system from TCA to MEC, chillers are required to contain the vapors, and a lip-vent exhaust or vapor-removal device may be necessary. The heat input should be reduced and carefully controlled to prevent too much agitation in the boiling solvent. The engineer in charge of surface cleaning should determine whether tighter equipment is required, or whether a retrofit is needed to minimize emissions.

Perchloroethylene (PCE)

PCE or perc (also known as tetrachloroethylene) is a clear, colorless liquid with a distinctive, somewhat ether-like odor. Physical properties of PCE include:

- Boiling point: 250 °F (121.1 °C)
- Freezing point: -9 °F (-22.8 °C)
- Vapor density: 5.76 times that of air
- Weight: 13.47 lb/gal

With the highest boiling point of the chlorinated solvents, PCE is excellent for removing heavy grease and high-melt waxes. It also easily removes moisture from wetted parts. With its high solvent power, it provides extensive cleaning action.

PCE is recyclable and can be readily recovered by carbon adsorption methods. It can also tolerate relatively large quantities of water without degrading. Because it vaporizes at a higher temperature than the other chlorinated solvents, however, higher utility costs are required for heating the solvent to vapor level and for cooling chill water above the vapor level in the degreaser. In addition, when cleaned parts are removed from the degreaser, they must be allowed to cool before they can be handled.

Trichloroethylene (TCE)

TCE is a clear, heavy liquid (12.11 lb/gal) with excellent solvency. Noncorrosive and easily recycled, 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. Carbon adsorption recovery is often used with TCE to trap emissions.

At one time, TCE had been the preferred solvent in the metal finishing industry, but numerous state and local environmental regulations now classify it as a VOC. As a result, it had been widely replaced with 1,1,1-trichloroethane, although TCE remained in use for specialty applications, such as stripping semi-cured varnish or paint films and removing heavy rosins and buffing compounds. With the phaseout of TCA, however, and the impetus of EPA's SNAP ruling, trichloroethylene is making a comeback.

Table 1
OSHA Permissible Exposure Limits (PELs)

Solvent	8-hr time-weighted average (TWA)—ppm	Short-term exposure (STEL)—ppm
Methylene chloride	500*	Acceptable ceiling concentration: 1000 Maximum acceptable peak: 2000*
Perchloro-ethylene	25**	—
Trichloro-ethylene	50**	200**
1,1,1-trichloro-ethane	350	450

*Currently under rulemaking to lower the PEL; 25 ppm has been proposed on an 8-hr TWA, with a STEL of 125 ppm.
**These limits in OSHA's 1989 rule have been overturned.

Table 2
ACGIH Threshold Limit Values

Solvent	8-hr time-weighted average (TWA)—ppm	Short-term exposure (STEL)—ppm
Methylene chloride	50	—
Perchloro-ethylene	25	100
Trichloro-ethylene	50	100
1,1,1-trichloro-ethane	350	450

Because of its excellent cleaning properties and high solvency, TCE has been considered the universal vapor-degreaser solvent. It is commonly used in vapor degreasers, is recyclable, dries quickly and has low energy requirements.

Conversion from TCA to TCE is fairly straightforward. Heat in the degreaser should be increased to 15 lb of steam, or equivalent electric or gas heat input, and all possible methods of emission reduction should be used to meet the lower PEL. Regular vapor monitoring is suggested to help keep the workplace within Occupational Safety and Health Administration (OSHA) limits.

Health Profile

One major benefit of chlorinated solvents is the extensive study that has been done on their safety and health effects. Extensive laboratory and epidemiological studies have been made, and these have resulted in well-documented exposure guidelines and safe handling procedures.

Exposure to vapor concentrations within recommended guideline levels will not result in any known adverse effects on most people. Acute overexposure to vapors, however, may cause anesthetic or narcotic effects (known as *solvent drunkenness*), central nervous system effects, and liver and/or kidney problems. Because chlorinated solvent vapors are heavier than air, very high concentrations can accumulate in poorly ventilated areas. Exposure to such concentrations can cause dizziness, unconsciousness, and even death.

Small amounts of chlorinated solvents that might be ingested inadvertently are not likely to cause injury. Ingestion of larger amounts, however—accidentally or intentionally—could result in serious injury or death. Occasional, brief skin contact with chlorinated solvents is not likely to produce any significant adverse effects, nor is a single, prolonged exposure likely to result in absorption of harmful amounts through the skin. The solvents can de-fat the skin, however, which can cause dermatitis to develop, especially when there is frequent gross daily contact.

In February 1995, the International Agency for Research on Cancer (IARC) reclassified perchloroethylene and trichloroethylene to Category 2A (probably carcinogenic to humans). PCE previously had been classified in Category 2B (possibly carcinogenic to humans), and TCE in Group 3 (not classifiable as to carcinogenicity in humans). The reclassification was based on the conclusion by the IARC panel of experts that laboratory studies provided sufficient evidence of carcinogenicity in animals, and that epidemiology studies provided limited evidence of carcinogenicity in humans. The experts, however, were not unanimous in their decision.

It should be stressed that this IARC evaluation is one of cancer "hazard," not "risk." While hazard reflects the intrinsic properties of a product, risk represents the possible health impact from exposure levels in practice. The IARC decision is not expected to have significant impact on users of PCE or TCE, provided appropriate safe-handling precautions are observed. It is The Dow Chemical Company's contention that the solvents can be used safely, as long as users follow the recommended exposure limits, which were established by taking into account the relevant data on both hazard and risk.

When IARC's monograph is officially published, the producers of the solvents are expected to make appropriate changes to the material safety data sheets (MSDSs) and labels for perchloroethylene and trichloroethylene. In addition, both the producers and their trade associations will investigate the need for additional research and independent reviews of existing and new laboratory and epidemiology studies.

Safety Guidelines

Permissible exposure limits (PELs), set by OSHA (Table 1), and recommended threshold limit values (TLVs), established by the American Conference of Governmental Industrial Hygienists (ACGIH) (Table 2), have been in force for chlorinated solvents for a number of years. In 1989, OSHA proposed a downward revision of the workplace PELs for a number of substances, including perchloroethylene and trichloroethylene.

This ruling was overturned in 1992 by the U.S. Court of Appeals for the Eleventh Circuit, sending workplace standards back to the limits set prior to 1989, at least until OSHA could develop a new standard. Dow recommends controlling exposure to the chlorinated solvents below OSHA's 1989 PELs, or the ACGIH guidelines, whichever is lower.

The chlorinated solvents are practically non-flammable, because they have no flash point or fire point as determined by standard test methods. Methylene chloride and trichloroethylene, however, do have a flammable range when high concentrations of vapors are mixed in air and exposed to a high energy source. Perchloroethylene has no flammable mixtures in air. Lower and upper flammability limits for methylene chloride in air at 77 °F (25 °C) are 14 to 22 percent, while the flammable range of trichloroethylene runs from 8 percent to saturation, with the saturation point increasing with temperature. At 100 °C, the upper flammability limit is 44 percent.

Before analytical methods were developed to detect chlorinated solvents in parts-per-million (ppm) and smaller quantities, it was considered safe to dispose of solvent wastes in landfills. Such practices are no longer acceptable. Today, the preferred method of disposing of solvent waste is to send the material, via a permitted waste-hauler, to a licensed reclaimer or a permitted incinerator, in compliance with federal, state and local regulations. Most states and the federal government now have regulations for the disposal of solvent wastes.

To promote the safe use and responsible handling of products in the chlorinated solvent family, U.S. producers of chlorinated solvents participate in the Responsible Care® initiative of the Chemical Manufacturers Association, including the initiative's extensive product and environmental stewardship provisions. This includes providing customers with safety, handling, storage, and disposal information, MSDSs, regulatory and environmental information. In addition, they may provide product literature and videotape training presentations.

EPA's SNAP Rule

EPA's new SNAP rule gives industry the official go-ahead to consider MEC, PCE and TCE as acceptable alternatives to TCA. Published on March 18, 1994, in the *Federal Register* (59 FR 13044-13161), the rule applies to the uses of TCA in surface cleaning, aerosols, adhesives, coatings and inks.

At the same time, EPA expresses concern about worker exposure and environmental emissions if these solvents are not used and controlled properly. They advise that the three chlorinated solvents should only be used in accordance with other environmental, workplace and consumer regulations. (See accompanying sidebar.)

Conversion Checklist

Anyone planning to use MEC, PCE or TCE as replacements for TCA in a vapor degreasing process should be careful to observe the following procedures:

1. Prior to conversion, be sure to obtain state and/or local air permits (VOC and air toxics), arrange waste disposal complying with all appropriate regulations, and make provisions to control worker exposure to solvent vapors below the OSHA PEL standard.
2. Drain and clean the degreaser. *Solvent must be removed completely to avoid instability from mixing solvents.* Entry into the degreaser should be avoided. If entry is required, it is critical to follow a confined-space entry procedure, such as described in ASTM Standard D4276.
3. If the existing solvent in the degreaser has gone acid, consult the solvent supplier for special cleaning procedures.
4. Adjust the vapor safety thermostat to activate (*i.e.*, to turn off the heat supply) when contacted by solvent vapors.
5. Adjust the boiling sump thermostat to activate at the approximate boiling temperature of the new solvent with 25–30 percent mineral oil content.
6. Prior to initial start-up:
   A. Review the MSDS
   B. Label the degreaser appropriately

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Table 3
Recommended Equipment Settings*

Solvent	Vapor safety thermostat (°F)	Boiling sump thermostat (°F)	Operating steam pressure (psig)
Methylene chloride	95	108	<2
Perchloro-ethylene	180	257	45–60
Trichloro-ethylene	160	193	10–15
1,1,1-trichloro-ethane	130	172	1–6

*__Note:__ While these are recommended equipment settings, users should always first consult with the machine manufacturer and current product literature before operating any machine.

7. Close all drains. Charge the degreaser to normal levels and start-up according to standard operating procedures.
8. Monitor worker exposure to ensure PELs are met.
9. For equipment adjustment, see Table 3 for thermostat and steam pressure settings.

The Degreasing NESHAP

Emission standards for chlorinated solvent degreasing operations are now governed by the new National Emission Standards for Hazardous Air Pollutants (NESHAP) for new and existing halogenated solvent cleaning operations. Issued by the U.S. EPA on December 2, 1994, the standards cover both vapor degreasing and cold (or immersion) cleaning with trichloroethylene, perchloroethylene, methylene chloride and chloroform, as well as with 1,1,1-trichloroethane and carbon tetrachloride, which are scheduled for phaseout as of the end of 1995. The goal of the NESHAP is an overall reduction in solvent emissions of 50–70 percent of current nationwide emissions.

Recognizing the great variety of industries using chlorinated solvents for cleaning, as well as the number of different applications and operating procedures, EPA has provided for a variety of options that companies can select to comply with these regulations. At the same time, the standards, which are set out in the *Federal Register*, are very complex.

Among other requirements, the NESHAP lists a number of control procedures. Various combinations of these can be used to achieve the required vapor emission limits. The user should consult *Federal Register*, Vol. 59, No. 231, pp. 61801–61820. The control procedures listed in the NESHAP are:

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—A refrigerated system that creates a cold-air blanket above the vapor zone.

Reduced room draft—Wind speed above the freeboard must not exceed 50 ft/min (15.2 meters/min).

Working-mode cover—Any cover or machine design that shields the cleaning machine from outside air disturbances during cleaning.

Dwell—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.

Carbon adsorption equipment—Equipment in the ventilation system connected with the degreaser.

In addition, operators must employ automated parts-handling, as well as specified work practices. The parts-handling system must be an automated hoist or conveyor that carries parts at a controlled speed of 11 ft/min or less through the complete cleaning cycle. The work practices, which have been set to reduce emissions, are listed in a qualification test developed by EPA, which cleaning machine operators must be able to pass.

EPA's guidelines as listed in the degreasing NESHAP provide excellent guidance for the safe and responsible use of chlorinated solvents in metal cleaning. Close adherence to these guidelines, as well as to other regulations, will permit companies to continue using the vapor degreasing process for high-quality cleaning of metal parts.

For assistance in implementing these guidelines, one of the chlorinated solvent suppliers will be able to help. ❑

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A Summary of Regulations Covering Chlorinated Solvents

Although the chlorinated solvents methylene chloride (MEC), perchloroethylene (PCE) and trichloroethylene (TCE) are not subject to phaseout as depleters of stratospheric ozone, they are subject to a variety of other federal, state and local regulations. Here is a summary of the major ones:

The Clean Air Act Amendments of 1990

VOC Regulations

TCE is controlled as a volatile organic compound (VOC), and limitations are placed on its emissions, particularly in ozone non-attainment areas. PCE is considered a VOC under most state regulations implementing the national ambient air quality standards for ozone. It does not contribute appreciably to smog formation, however, so the U.S. EPA is expected to grant it exemption fromVOC regulations. MEC is exempt from both federal and state VOC regulations.

HAP Regulations

EPA has designated the chlorinated solvents as hazardous air pollutants (HAPs). A complete set of regulations has not been issued for their control, although a National Emission Standards for Hazardous Air Pollutants (NESHAP) has been issued for cleaning with chlorinated solvents.

Many states have enacted HAP regulations or Toxic Air Containment (TAC) regulations for lists of chemicals, which usually include chlorinated solvents.

Occupational Safety & Health Administration (OSHA) Hazard Communication (HAZCOM)

Training on hazardous chemicals in the workplace is required for all employees who could be exposed to the chlorinated solvents, including annual refresher courses. Containers of these hazardous chemicals in the workplace, as well as containers leaving the workplace, must be marked with an "appropriate hazard warning label." In addition, individual states—including California, New Jersey, New York and Pennsylvania—have specific labeling requirements.

Resource Conservation & Recovery Act (RCRA)

Waste containing chlorinated solvents must be considered hazardous waste. It must be transported by a certified hazardous waste hauler, stored in a licensed storage facility, and disposed of in licensed treatment and disposal facilities.

Comprehensive Environmental Response, Compensation & Liability Act (CERCLA or Superfund)

If a "reportable quantity" of a chlorinated solvent is released to the environment in any 24-hr period, federal, state and local authorities must be notified immediately. Reportable quantities for each of the solvents are: Methylene chloride, 1000 lb; perchloroethylene and trichloroethylene, 100 lb.

Clean Water Act

The chlorinated solvents are defined as toxic pollutants (also called priority pollutants), and their discharges into waterways are regulated. Different regulatory requirements may be demanded of *direct* dischargers (those that discharge directly into a waterway) and *indirect* dischargers (those that discharge into a water treatment system).

In addition to federal requirements, state and local governments may have specific regulations concerning the discharge of wastewater containing these solvents. ❑