Metal Cleaning with 1,1,1-Trichloroethane

PD

by J.A. Mertens
The Dow Chemical Co., Midland, MI

Metal cleaning or degreasing is an essential part of the modern production process, particularly in industries fabricating or assembling metal parts. These include manufacturers of parts for air and spacecraft, appliances, automobiles and trucks, electronic equipment and railroad stock. This process, in which the metal part is subjected to the action of a solvent, is used to remove oils, waxes and fluxes that adhere to the metal during production and machining, and oil borne soils such as chips and metal fines.

Solvents used in metal cleaning are subject to a number of state regulations governing air quality, and both federal and state regulations governing worker health and safety and the disposal of wastes. This has led many manufacturers to reassess their metal cleaning operations, often with a view to making changes that will bring them into compliance with new regulations.

Fortunately, compliance is not difficult, and is often less costly than is often thought. In many cases, the use of 1,1,1-trichloroethane, also known as methyl chloroform, has proven to be the solution to compliance problems. In the following paragraphs we will review the various procedures used in metal cleaning to see where this compliance solvent fits.

DEGREASING METHODS

Degreasing is a necessary stage in production because it prepares a metal part for further surface treatment, such as electroplating, painting, galvanizing, anodizing, or applying conversion coatings. It is also needed for cleanliness if the part is to be packaged with no further surface treatment.

A variety of degreasing methods are possible. The principal ones are cold cleaning, in which solvent is applied at room temperature or slightly heated and vapor degreasing in which solvent is boiled and the vapors condensed on the part.

In cold cleaning, the parts are immersed and soaked in a solvent bath. Parts too large to be immersed can be sprayed or wiped with the solvent. This process is most often used for maintenance applications, such as tool cleaning, and periodic cleaning of small quantities, although some large volume production processes may also use cold cleaning.

An alternate to cold cleaning is an aqueous alkaline wash. This requires a rinse after cleaning, and is not as effective as a solvent bath for many operations.

Vapor degreasing is usually more economical and satisfactory for large volume processes, and it has the added advantage that it does not reapply dissolved soils to the part being cleaned. A cold solvent bath may become contaminated with soil from previous work. This may cause soil redeposition on subsequent parts being cleaned. In a vapor degreaser soils usually have a higher boiling point than the solvent, and consequently do not vaporize when the solvent is boiled. The part is exposed to clean solvent vapors prior to being withdrawn from the degreaser, ensuring a clean solvent rinse. Thus vapor degreasing results in a clean product that is already dry and consequently does not add the fumes of the evaporating solvent to the working environment.

In vapor degreasing, sufficient heat is applied to the cleaning solvent to boil it. The combination of high vapor density, cooling coils, freeboard chiller and freeboard maintains a solvent vapor zone well below the top of the tank, thus keeping the solvent vapors within the tank to clean the parts.

The dirty parts, or "the work", are lowered into the tank. On contacting the cold work, the vapor condenses into pure liquid solvent, which dissolves the grease and carries off the soil as it drains from the parts into the heated reservoir below. This process continues until the work reaches the temperature of the vapor. At that point, condensation ceases and the work can be lifted out of the vapor clean and dry.

VARIATIONS ON VAPOR DEGREASING

In cases where the work has insoluble abrasives and metal fines from buffing or polishing that remain after the vapor has removed the lubricants, a solvent spray can be used in addition to the vapor cycle. This process can also be used for small parts stacked in baskets, since solvent spray can break air pockets and reach enclosed areas. When the degreaser is equipped with a hand operated spray lance or fixed spray nozzles, the work is suspended in the vapor zone for initial cleaning and then sprayed with cool, clean solvent. This not only flushes out soils, it also lowers the surface temperature and permits further vapor condensation.

When the work has intricate contours and/or a heavy amount of soil, or when bulk quantities of small parts are covered with a light film of oil or grease, the work can be treated by immersion as well as vapor. Usually the parts are agitated or tumbled at the same time. In this process, a two-compartment degreaser is generally used, with a boiling-solvent sump for vapor production and a warm liquid chamber for immersion. The work is lowered through the vapor zone for preliminary cleaning, rotated or agitated in the warm liquid, and then raised into the vapor zone for final rinsing.

A variation on this is the multiple immersion process, in which the work is first lowered into the boiling liquid, where the boiling action adds to the mechanical agitation, and then into the warm rinse.

The interiors of enclosed vessels or tanks—tank transports, storage tanks and processing tanks—require a different degreasing method. They can be cleaned and dried by spraying with solvent distillate and vapor cleaned with vapor from a separate generator. The solvent is recycled between generator and tank until the cleaning is complete.

Ultrasonic cleaning is industry's most advanced application of the principle that agitation improves and speeds cleaning. When ultrasonic energy is transmitted to the solvent bath it produces cavitation—the rapid build-up and collapse of tiny bubbles. This imparts a scrubbing action to the surface of soiled parts. Scrubbing, teamed with the action of the solvent, results in highly effective cleaning which is especially effective on heavy oil deposits, insoluble solids, fluxes on printed circuit boards, and micro-sized contaminants on precision electronic components.

SELECTING A SOLVENT

To provide thorough, safe, economical and rapid metal degreasing, the ideal solvent should have a number of properties. Since different solvents possess these properties to different degrees, the specific needs of the cleaning operation often determine which solvent to select.

The most desirable properties are:

- *High solvent power:* the ability to dissolve all greases, fats, oils, waxes, resins, gums and rosin fluxes generally encountered in metalworking.
- *Inertness to metals and plastics:* the ability to clean the part without corroding, oxidizing, staining, etching, pitting, or dulling the work or the degreasing equipment.
- *Nonflammability:* the quality of performing at the elevated temperatures required for vapor degreasing without the danger of fire. Ideally, the solvent should have no flash point discernible by standard laboratory test methods.
- *Low toxicity:* a sufficiently low toxicity that the exposure likely to occur when the solvent is properly used will not impair the operator's health.
- *Low latent heat:* the ability to produce a high amount of vapor per unit of heat input, thereby minimizing the energy costs associated with vaporizing the solvent.
- *High density vapor:* a density heavier than air, so that solvent loss through work transfer and disturbance of the vapor will be minimal. This property also permits effective control of vapor level by means of condensing coils or thermostats in the upper region of the degreaser.
- *Chemical stability:* the ability to remain stable and effective in both the liquid and vapor phases after continuous and repeated operation. Solvents must be properly stabilized with chemical inhibitors to protect against reactive metal chips and fines, acidic heat, air, moisture and other metalworking contaminants.
- *Low boiling point:* a boiling point low enough for the solvent to separate easily from the higher boiling cutting oils, greases and other contaminants. Yet it should be high enough so that the condenser coils filled with cool plant water can keep the vapors down.
- *High vapor pressure:* to permit an effective evaporation rate both in the vapor degreaser and on the part being cleaned.

SOLVENTS TO CHOOSE FROM

A variety of solvents are used in metal cleaning and should be measured against these properties. Among the solvents most widely used in cold cleaning are chlorofluorocarbons, some alcohols, and aliphatic hydrocarbons such as mineral spirits.

In many cases, however, the chlorinated solvents—methylene chloride, perchloroethylene, trichloroethylene and 1,1,1-trichloroethane—are preferred. These are also the preferred solvents for vapor degreasing, along with the milder solvent 1,1,2-trichloro-1,2,2-trifluoroethane, more commonly known as fluorocarbon 113. The chlorinated solvents stand out in both cold cleaning and vapor degreasing because of their high solvency and excellent cleaning properties, the high density of their vapors, their safety and their nonflammability.

Each of the four chlorinated solvents has specific advantages for special applications.

Methylene chloride (CH_2Cl_2) has the highest solvent power of all the chlorinated solvents, and will remove tough paint residues and resins. Because it has the lowest boiling point of the four (104°F, 39.8°C), it is frequently used in cleaning temperature sensitive parts.

Perchloroethylene (C_2Cl_4), with the highest boiling point of the chlorinated solvents (250°F, 121.1°C), is recommended for dissolving contaminants with a high melting point, such as waxes. It is also used for cleaning wet parts.

Trichloroethylene (C_2HCl_3, boiling point 189°F, 87°C) was the preferred metal cleaning solvent until recently; however, tightening environmental controls have caused many users to replace it with systems in closer compliance with regulations. It is still widely used in specialty applications.

1,1,1-trichloroethane ($C_2H_3Cl_3$) has a gentler cleaning action than trichloroethylene and a lower boiling point (165°F, 74°C) than either trichloroethylene or perchloroethylene. These make it appropriate for cleaning items such as printed circuit boards, electric components and electric motors that might be damaged by high temperatures. Most importantly, however, it has a number of advantages that enable it to bring a metal cleaning operation into compliance with environmental regulations.

AN ECONOMICAL SOLVENT

1,1,1-trichloroethane is also economical. Because of its lower boiling point and lower weight per gallon than the popular TCE, as much as 40% lower solvent consumption has been reported. The lower boiling point also means that less heat is required to vaporize the solvent and less cooling to provide condensation in the degreaser. Cleaned parts are cooler, permitting more rapid handling and processing, while reduced heat radiation from the degreaser means a more comfortable working environment for the operator and less energy required to cool the area.

Since 1,1,1 can be used for both cold cleaning and vapor degreasing, a plant can minimize inventory by stocking a single solvent. In addition to being versatile, it is also a selective solvent: it will dissolve and clean metalworking soils but will not attack sensitive materials such as many plastics. Thus it is the chosen solvent for degreasing hermetic stators and printed circuit boards, where other solvents may damage insulation, cause heat warping, or remove identification.

The lower boiling point also makes 1,1,1 easy to recover by distillation. It can be efficiently distilled without steam stripping, thus saving on energy costs and avoiding water contamination. Distillation recovery improves operating economies and extends useful solvent life.

If a manufacturer decides to convert from TCE to 1,1,1, the changeover can be done economically. Only minor modifications are needed in existing TCE degreasers. These include reducing the heat input, readjusting the thermostats, and installing a properly sized water separator.

The major disadvantage of 1,1,1 is

its intolerance of excessive water. Degreasing operations with gross water contamination should not employ the solvent, although moderate or intermittent water contamination is handled effectively by an adequately designed water separator. In addition, 1,1,1 vapors should not be recovered by carbon adsorption, since this process depletes the stabilizers below the acceptable levels.

THE COMPLIANCE SOLVENT

Today manufacturers choosing a metal cleaning solvent must pay special attention to what environmental regulations apply. In recent years the nation as a whole has been moving towards more stringent air quality, worker safety and waste disposal regulations. One driving force behind the tighter guidelines is the growing concern over ozone generation — and attendant smog — caused by volatile organic compounds (VOCs) and other air contaminants. 1,1,1-trichloroethane offers a practical choice as a compliance solvent.

The EPA in 1977 categorized solvents by their rates of photochemical reactivity. Some solvents had such a low rate of reactivity that they were classified as having negligible impact in the formation of ozone. 1,1,1-trichloroethane was one of these; only the organic inhibitors, which are added to help stabilize the product and are present in quantities of three to five percent, are nonexempt.

Consequently, 1,1,1 is excluded from the VOC emission requirements of most State Implementation Plans (SIPs), except in Kentucky, New Jersey and Rhode Island. Michigan recently voted to exempt the solvent from air quality restrictions governing ozone control, but limited the exemption to use in industrial coatings. Pennsylvania also exempts 1,1,1 when used in coatings, but not in metal cleaning applications.

WORKER HEALTH AND SAFETY

From the point of view of employee safety, 1,1,1 is the easiest of the solvents to use. The eight-hour time weighted average (TWA) permissible concentration is 350 ppm by volume in air. This is accepted by both the Occupational Safety and Health Administration (OSHA) and the American Conference of Governmental and Industrial Hygienists (ACGIH), and it compares favorably with the limits of 50 ppm set by ACGIH for the other chlorinated solvents. Although OSHA has set limits for perchloroethylene and trichloroethylene of 100 ppm, The Dow Chemical Company recommends adhering to the lower ACGIH limits. OSHA's present limit for methylene chloride is 500 ppm, but advance notice has been issued of proposed rulemaking to revise this.

The health profile of 1,1,1-trichloroethane is extremely favorable. Health and safety information has been gathered over many years of industrial use and laboratory testing. For one thing, the solvent has no measurable flash point by standard test procedures, and its lower flammability limit is higher than most solvents.

Numerous health and toxicology tests, including a two-year "lifetime" inhalation test with rodents, have demonstrated that the solvent can be safely used if handled properly.

Naturally, reasonable precautions are required to ensure workers' health and safety. As an example, when 1,1,1 is used, the working environment should be well ventilated to minimize exposure. Over inhalation of the solvent can lead to an anesthetic effect, or solvent "drunkenness," creating a condition where industrial accidents can occur. When exposed to higher concentrations, workers can be overcome by solvent vapors and lose consciousness, and this may even lead to death. If any of these symptoms occur, the condenser coils in the degreaser should be checked in case vapors are escaping above the cool air blanket. Air supplied masks will allow workers to avoid solvent vapor during extreme exposure, as during a tank clean out.

Repeated, prolonged exposure of the skin to liquid solvent can be irritating and lead to dermatitis. To avoid irritation, polyvinyl alcohol, Viton, or butyl rubber gloves are recommended.

WASTE MINIMIZATION AND DISPOSAL

One of the major issues for a manufacturer with a metal cleaning operation is how to dispose of waste solvent in accordance with federal and state regulations. The Resource Conservation and Recovery Act (RCRA) lists all chlorinated solvents, including 1,1,1-trichloroethane, as hazardous wastes which must not be disposed of in landfills. The only disposal methods to be considered are recycling, fuel blending and incineration.

Any overall waste program, however, should begin with waste reduction and minimization. This makes good economic sense, of course, as well as good environmental sense.

Several solvent conservation techniques are recommended to prevent solvent loss and keep the plant atmosphere clean. One very simple procedure, yet the single most effective one, is to cover the degreaser during nonuse and idling intervals. Considerable losses can occur from uncovered idling degreasers due primarily to molecular and thermal diffusion and convection. Covers can be constructed from low cost, lightweight materials. When designed to slide on and off, they can be opened without causing turbulence in the solvent vapor zone.

Keeping turbulence under control is another way of keeping solvent vapors from escaping from the degreaser. This can be done by keeping the solvent at a slow boil (incidentally, a good economic practice, too); preventing air movement from fans, open doors and windows, or even negative building pressure; keeping solvent spray below the cooling coils; and by keeping movement of work loads in and out of the degreaser at a speed below 11 feet per minute.

In addition, a cool freeboard area prevents convection currents which can carry solvent vapors out of the degreaser. Dragout of solvent as parts are removed from the degreaser can be minimized by arranging parts so that holes, troughs and pockets will drain freely. Above all, the work should not be removed from the degreaser before vapor temperature is reached and the parts become dry.

One additional cause of vapor loss is excessive moisture in the degreaser; this lowers vapor density and permits solvent vapors to rise too high. If this problem exists, a more effective water separator may be called for.

RECYCLING SOLVENT

The most effective tool for waste minimization is recycling of spent solvent. This can be accomplished both on-site and off-site through a commercial recycler. Solvent can be recycled on-site either in a separate still or by a distillation technique in the degreaser called a "boil down". Either method recovers clean solvent for reuse, reducing the volume of waste that needs to be disposed of.

A total on-site recycling process is not always the most cost efficient waste reduction method. In addition, many manufacturers may find help in outside services. Some solvent distributors will give credit for recoverable solvent when they pick up sludge; then they process the waste solvent and end up with clean, recovered solvent for return or resale, and a waste sludge which they will dispose of in a responsible manner.

Nearly all commercial reclaimers have arrangements with large fuel blenders to dispose of the solvent sludge from reclaim processes as waste derived fuel for cement kilns, aggregate furnaces, blast furnaces, or large utility or industrial boilers. Dow does not endorse the disposal of chlorinated solvent waste in landfills or deep wells.

When a manufacturer purchases reclaimed solvent from a processor, he should obtain a complete analysis o the product. One thing to be careful o is the stabilizer level. Stabilizers shoul be in the proper ratio, between 3 an 5% by weight, and provide sufficien acid acceptance and metal stability. Excess stabilizer can produce a flammability hazard or increase the VO count, while insufficient stabilizer ca shorten the solvent life. Water conten should be low, below 220 ppm fo 1,1,1, otherwise solvent life can b shortened and vapor loss increased.

Any reputable hazardous waste treatment company will answer question on their operations, the analysis of recycled solvent and the disposal of wast sludge. In fact, a responsible compan will offer full information as proof o their capabilities. A manufacture should be careful to contract for wast recycling and disposal services onl with firms which respond satisfactoril to questions on the disposal cycle a well as on their compliance with fed eral, state and local regulations. MF