CHOICES AND SOLUTIONS

NEWSLETTER

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Important News For Dow's Chlorinated Solvents Customers

Alternatives To Chlorinated Solvents

The metal cleaning process was a relatively open and shut matter at one time: unless you had specific reasons to specify something else, vapor degreasing was the process of choice and chlorinated solvents or chlorofluorocarbons (CFCs) were the solvents of choice. This all changed at the end of 1995, when the most popular solvents, 1,1,1-trichloroethane and CFC 113, were classified as ozone depleting substances (ODSs) and phased out of production for all applications (other than as chemical intermediates) in the developed countries. Today, manufacturers are faced with a bewildering number of alternative choices in both chemistry and methodology.

As we have pointed out in these newsletters, the solvents which come closest to being drop-in replacements for the phased-out products are the chlorinated solvents, trichloroethylene (TCE), perchloroethylene (PERC), and methylene chloride (MEC). These solvents have an excellent combination of high solvency, high cost effectiveness, a long history of proven safe use practices, and extensive health studies.

At the same time, a large number of products and technologies are being offered to industry as alternatives to the chlorinated solvents, and are often promoted on the basis of health, safety, environmental, and economic advantages. Let's look at some of the available alternatives, and examine how they stack up against the chlorinated solvents.

Aqueous Cleaning

This process, which uses a detergent-water or an alkaline chemical solution, is an extremely popular cleaning method today. Although not always as effective at removing grease and oils to the same levels of cleanliness which vapor degreasing provides, in cases where precision cleaning is not required, aqueous cleaning often provides sufficient cleaning to meet the needs. Aqueous systems are usually designed to handle specific cleaning needs, and chemical, thermal, mechanical or ultrasonic energies can be added as required. These systems present few problems with safety or the environment, although water treatment is generally required to dispose of spent solutions and rinse water.

Disadvantages of alkaline washing, as compared with chlorinated solvents, include the following:

- It is difficult to clean crevices and small holes with aqueous solutions. Chlorinated solvent vapors, however, are able to reach all regions of the most convoluted parts.
- To be effective, an aqueous process must be carefully engineered and controlled. On the other hand, chlorinated solvent vapor degreasing is a forgiving process.
- In addition to the washing stage, an aqueous process requires a rinsing and often a drying stage. Although a simple aqueous line may appear to be more economical to run than a vapor degreaser, the energy required in heating water and in the drying stage makes an aqueous line more costly and energy consuming than vapor degreasing. This multi-stage process also requires more floor space than a vapor degreaser.
- Unless an aqueous line is carefully maintained, as work proceeds, washing and rinsing tanks may become contaminated with soils which can be redeposited on parts. Thus it is necessary to maintain a clean solution at all times. In vapor degreasing, the chlorinated solvent vapor is free of contaminants and invariably leaves the part clean. Even when the cleaning process includes a stage where the part is submerged in the solvent, the final stage always takes place in clean solvent vapor.

Semi-Aqueous, or Emulsion Cleaning

A semi-aqueous line works much like an aqueous line. Initially the parts are exposed to a non-chlorinated solvent, which usually incorporates a surfactant. In the second step, they are immersed in an emulsion bath, where the solvent is mixed with water and held in suspension by the surfactant and by agitation. The surfactant helps remove residual solvent from the parts, and with it residual oils, carrying them into the aqueous phase. The emulsion bath is continuously cleaned, allowing the solvent phase to be returned to the solvent tank and the water to the emulsion tank. The

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remaining steps are the same as in an aqueous line-rinsing and drying.

This process can provide good cleaning, with suppressed vapor. The disadvantages include the following:

- Recycling is often difficult. The solvent used in the process is usually a hydrocarbon-based material, and cannot be distilled easily without special equipment. When oil contamination reaches the neighborhood of 30 percent, the solvent usually has to be replaced. Chlorinated solvents, on the other hand, are continuously distilled in a vapor degreaser, and can easily be concentrated to mixtures of more than 60 percent oil in conventional single-step stills.
- Most solvents used in emulsion cleaners are either flammable or combustible. Where these are used, special equipment must be employed to protect against fire. The chlorinated solvents are considered non-flammable, because they have no flash point according to standard test methods†.
- Most of the solvents used in emulsion cleaners are volatile organic compounds (VOCs), which contribute to the formation of smog and must be carefully controlled. Of the chlorinated solvents, both PERC and MEC are exempt from VOC regulations.
- Like aqueous cleaning, semi-aqueous cleaning requires rinsing and often drying stages. Thus a semi-aqueous cleaning line will require more floor-space and energy than a vapor degreaser.
- Not all emulsion cleaners have been fully researched for their toxicity. The chlorinated solvents are among the most fully studied and best understood industrial chemicals currently on the market.
- Some emulsion cleaners have specific problems of their own, such as gelling in low-water-content solutions, or auto-oxidation. These effects should be examined before specifying the process.

†See the relevant Material Safety Data Sheet.

Other Cleaning Processes

In addition to aqueous and semi-aqueous cleaning processes, a number of other cleaning processes are on the market. These include:

Non-Chlorinated Solvents, such as acetone, mineral spirits, n-methylpyrrolidone (NMP), and terpenes. Although these can often provide good cleaning, they are flammable or combustible, making them unsuitable for vapor degeasing and restricting them primarily to limited cold cleaning applications such as wipe cleaning or simple immersion. The evaporation rate (drying time) is often a problem; they are either too slow, requiring extra time for drying, or too fast, requiring more product to clean the parts.

In addition, a number of new “designer” solvents have been developed, such as volatile methyl siloxanes, oxygenated solvents (glycol ethers and dibasic esters), the hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs), and n-propyl bromide.

Methyl siloxanes were introduced on the market recently. These products are very good at attacking silicone-based oils and lubricants, and in some cases, coatings. They are flammable, however, so they must be used in a process which suppresses the flammability.

While the oxygenated solvents offer excellent solvency properties, they are also flammable or combustible, and so unsuitable for vapor degreasing. They are frequently used as components of semi-aqueous formulations, and even some aqueous formulations, although in some areas the amounts used in the formulations may be limited due to VOC requirements.

The HCFCs, HFCs, HFEs and n-propyl bromide were developed as attempts to imitate the chlorinated solvents. In these cases, a halogen (chlorine, fluorine, or bromine) is attached to a hydrocarbon backbone to reduce flammability. Fluorine is the most frequently selected halogen, and fluorinated products generally have low toxicity and minimal effect on the environment.

These advantages, however, are offset by their lower performance and higher cost than the chlorinated products. In particular, the solubility parameters of the fluorine-based solvents is usually low, making them ineffective for metal cleaning. Frequently a more aggressive additive is blended in, such as 1,2 trans dichloroethylene (a chlorinated solvent) or alcohol. The cost of the designer solvents is 12 to 15 times the cost of the traditional chlorinated solvents. This means that it is even more important to minimize waste, and this generally results in more expensive equipment.

N-propyl bromide is a recent product offering which was previously overlooked because of its potential flammability. Recent tests, however, show that the flash points reported in the literature are outside the temperature ranges of the current standard test procedures. Little toxicological study has been made on this product, and it will be several years before an extensive knowledge base is available. Initial indications are that it will probably require worker exposure limits similar to those of the chlorinated solvents. There are also unresolved questions as to its ozone depletion potential (ODP), environmental impact, and health effects.

Supercritical Fluids (SCF). These products are receiving a good deal of publicity in today's industrial press, in particular supercritical carbon dioxide (CO_2), which is reputed to have excellent cleaning properties and little environmental impact. SCFs are fluids which may be either gaseous (like CO_2) or liquid (like water) at ambient temperatures and pressures, but reach a supercritical stage when compressed and heated beyond their critical pressure and temperature. In the case of CO_2, the critical temperature is 31.1°C and the critical pressure is 73.9 atmospheres. Such pressure requires costly equipment with safety features. Obviously, considerable equipment development is still needed before this process can be generally applied.

Miscellaneous. A number of other cleaning processes under discussion may merit further examination. These include plasma cleaning, laser cleaning, thermal vacuum cleaning, and mechanical cleaning.

Plasma and laser processes require a high investment in equipment. The thermal vacuum process is an excellent means of removing oils by evaporation, but it has little effect on metal fines or other forms of soil which may get on parts during fabrication.

Mechanical cleaning through blasting the part with a medium such as pressurized gas, dry ice pellets, or starches, may be right for specific cleaning processes. Its major disadvantages include the special handling required to clean all surfaces of a part, and potential damage to the part. In addition, if the process removes grease and oil, the media becomes clogged with the soils, requiring extensive recycling methods or frequent replacement of the media.

The Chlorinated Solvents

Reviewing all these alternatives, it is obvious that each has its advantages and disadvantages. Each may be appropriate for some cleaning applications, but inappropriate for others.

The same can be said of vapor degreasing with chlorinated solvents. No other cleaning technology provides the same combination of high solvency, high precision cleaning, cost effectiveness, low flammability, and limited floor space. At the same time, health and environmental regulations in North America and Western Europe require careful control of emissions to attain extremely low workplace exposure levels. Waste products from chlorinated solvent cleaning processes are regulated as hazardous waste and must be disposed of in accordance with regulations. In addition, trichloroethylene, the chlorinated solvent with the broadest applications, is classed as a VOC, and additional controls may be placed on emissions in air quality non-attainment areas.

The good news for chlorinated solvent users, however, is that a great deal of help is available from solvent producers to assist in meeting regulatory standards. The Dow Chemical Company provides customers with a library of helpful literature and other forms of assistance, including:

- A product stewardship manual detailing safe handling and disposal procedures, as well as physical and chemical data on the products.
- An illustrated safety brochure for operating personnel, "How to Get Along with Solvents," and a safe handling wall poster for the plant. The brochure is available in both English and Spanish, while the poster uses pictograms to aid comprehension across language barriers.
- A waste reduction kit containing literature on waste reduction and minimization.
- A vapor degreasing kit containing literature on economical and efficient vapor degreasing methods, as well as procedures for converting surface cleaning lines to chlorinated solvents.
- The Choices and Solutions newsletter for both direct customers and customers of distributors. This contains information on federal and state regulations as well as tutorial articles on safe and responsible use of the solvents.
- The development of a closed-loop solvent transfer (CLST) system for both delivery of solvent to the customer's equipment and the removal of waste solvent for disposal/recycle. A special vapor return capability permits solvent transfer with virtually no emission of vapors to the atmosphere and little chance of solvent spills.

In addition, workplace vapor monitoring badges are available to customers, as well as test kits to measure the quality of the inhibitors in the solvents. Dow's Technical Service and Development (TS&D) personnel are also available to advise customers and help them comply with regulations.

The Halogenated Solvents Industry Alliance (HSIA), an association of producers and users of chlorinated solvents, also provides literature on these solvents as well as an informative newsletter. Information can also be obtained on the organization's website, www.hsia.org, or by calling HSIA at 202-775-0232.

For information on these forms of assistance, speak to your distributor of Dow chlorinated solvents, call Dow at 1-800-447-4DOW (4369), or visit Dow's chlorinated solvents website, www.chlorinatedsolvents.com.

Economics of Cleaning Systems—A Comparison

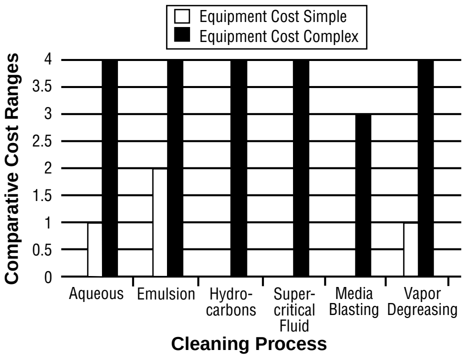

Chart 1. Equipment Cost Comparison

Cleaning equipment can range from simple units such as a small open-top degreaser (the base line, or 1) to a fully enclosed automated unit with no solvent-air interface. Other systems, by comparison, will often require higher capital costs.

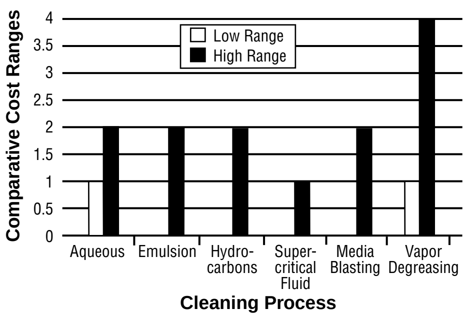

Chart 2. Chemical Cost Comparison

For vapor degreasing, the chlorinated solvents are the base line, with certain non-chlorinated solvents representing the higher cost (see Chart 5). Other chemicals may show low unit cost, but the associated use costs are usually higher.

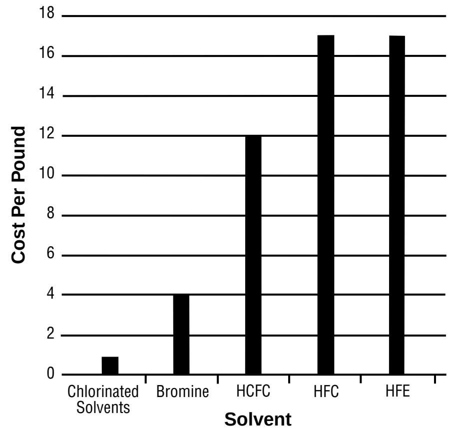

Chart 3. Comparative Vapor Degreasing Solvent Costs

Average cost of chlorinated solvents forms the base line, with some alternative solvents running as much as 17 times as high.

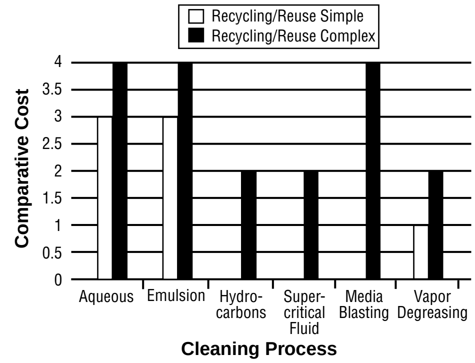

Chart 4. Recycling and Reuse Cost Comparison

For vapor degreasing, the cost of recycling the chlorinated solvents is the base line, with the higher column representing the cost of recycling certain non-chlorinated solvents.

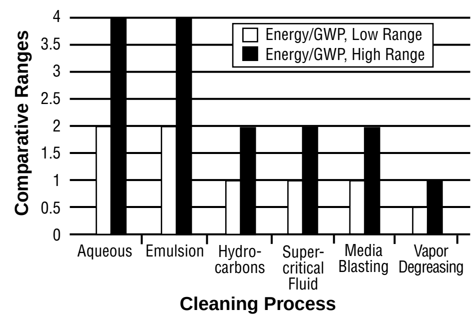

Chart 5. Energy and Global Warming Effects

For vapor degreasing, the energy requirements and global warming potential of chlorinated solvent use are the lowest of any cleaning system.

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