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AQUEOUS ALTERNATIVES FOR METAL AND COMPOSITE CLEANING

by

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The Problem

For many years the metalworking industry has cleaned metal and composite substrates with chlorinated solvents. Recently, however, health and disposal related environmental concerns have increased regarding chlorinated solvents, including 1,1,1-trichloroethane, trichloroethylene, methylene chloride, or Freon[1]. World leaders have instituted a production ban of certain ozone depleting chlorofluorocarbons (CFC's) by 1996.

The Occupational Safety and Health Administration (OSHA) has instituted worker vapor exposure limitations for virtually all of the solvents used in solvent-based cleaners. In addition, the United States Environmental Protection Agency (EPA) has defined nearly all solvent-based cleaners as *"hazardous"*. Cradle to grave waste responsibility is another reason manufacturers are trying to replace chlorinated solvents in their cleaning processes.

Because of these factors, there now is a world wide effort to reduce and/or eliminate the use of chlorinated solvents for industrial cleaning.

Waterbased cleaners are among the alternatives being offered to the industry. New technology alkaline cleaners are now available that can be used instead of chlorinated solvents in many cleaning processes. These waterbased cleaners reduce the release of volatile organic compounds (VOC's) by as much as 99 percent. *(The definition and method of calculation of VOC's now varies from region to region.)* Hazardous waste generation can also be significantly reduced or eliminated with new aqueous technology. This in turn can ease worker exposure restrictions and positively impact the environment.

TABLE 1
PHYSICAL PROPERTIES OF VAPOR CLEANERS

Parameter	A	B	C	D
Boiling Point (°C)	39.8	74.1	86.9	121
Boiling Point (°F)	104	165	189	250
Specific Gravity	1.316	1.322	1.456	1.613
Flash Point (TOC) °C	none	none	none	none
Vapor Pressure,mm	340	90	59	13
Volatile Organics (VOC) #/gallon	10.98	10.92	12.11	13.47
Surface Tension (dynes/cm)	28	28	28	28

CODE: A= Methylene Chloride
B= Trichloroethane (TCA)
C= Perchloroethylene (PERC)
D= Trichloroethylene (TCE)

The use of aqueous products can also eliminate or reduce the annual reporting required[2] under SARA Title III, Section 313 (*Toxic Chemical Release Reporting: Community Right-To-Know*) because these aqueous cleaners contain little or no (less than 5%) chemicals currently listed in Section 313. Standard degreasing solvents such as perchloroethylene, methylene chloride, trichloroethylene, and Freon presently require reporting under Section 313 when used in quantities of 10,000 pounds or greater annually.

Tables 1 and 2 compare the physical and chemical properties of waterbased cleaners versus chlorinated solvents.

TABLE 2
PHYSICAL PROPERTIES OF AQUEOUS CLEANERS

Parameter	A	B	C	D
Boiling Point (°C)	100	100	100	100
Boiling Point (°F)	212	212	212	212
Specific Gravity	1.02	1.07	1.07	1.02
Flash Point (TOC)°C	none	none	none	none
Vapor Pressure, mmHg	29	23	23	18
Volatile Organics (VOC) #/gallon	0.2	0.0	0.0	0.5
Surface Tension (dynes/cm)	29	29	33	32
pH, 100%	11.5	13.0	13.0	7.8
pH, 10%	10.5	12.0	11.7	7.1

Cleaning Process Defined

Cleaning is defined as *"the removal of soil or unwanted matter from a surface"*.[3] There are a wide variety of cleaning processes to choose from depending on the nature of the soil, the substrate involved and the degree of cleanliness required.

Cleaning of metal and composite substrates can be accomplished in several ways: 1) by using mechanical action such as wiping, brushing or spraying; 2) by solubilizing the soil; 3) by chemically reacting the soil through saponification or chelation; or 4) by lifting the soil through surface action and detergency. Often a combination of mechanisms is employed.

Solvent Degreasing

Vapor degreasing[4] has been a traditional means to clean industrial components. During this cleaning process vapors from a boiling solvent condense on the cooler part, flushing off oily soils. The soils are then dissolved in the solvent. This cleaning action continues until the part warms up enough to stop the condensation from occurring. At this time the cleaning process is complete whether the parts are clean or not, generally within ten minutes. The part is then removed from the degreaser tank clean and dry. A spray wand may be used to remove particulate soils not readily removed by the vapors.

Chlorinated solvents most frequently used for vapor degreasing include: 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), perchloroethylene (PERC) and methylene chloride. Freon is also used, especially by the electronics industry.

Vapor degreasing is an effective method for removing organic soils such as oil-based cutting oils, greases, petrolatums and high-melt waxes. It is less effective in removing inorganic soils like fingerprints, water salts and road film. Aerospace, electronics and automotive industries have typically employed vapor degreasing methods for cleaning.

Once a hydrocarbon solvent has been used for degreasing purposes, it must be redistilled in order for it to be reused. This can require a significant capital equipment expense. More often than not, the resulting sludge and/or used solvent is discarded and treated as hazardous waste.

Some waterbased cleaners contain non-chlorinated solvents as part of the package. These semi-aqueous emulsion cleaners contain hydrocarbon solvents and emulsifiers. Since they contain non-volatile residues, water rinsing is generally required. These emulsion cleaners work by solubilizing and/or emulsifying the soils and dispersing them throughout the bath. As the semi-aqueous cleaner is used, the entire bath becomes contaminated. The entire bath, including the water and any water rinses, must be treated as hydrocarbon waste. Again, the waste generator is legally responsible for that waste "from cradle to grave".

New Technology Aqueous Cleaners

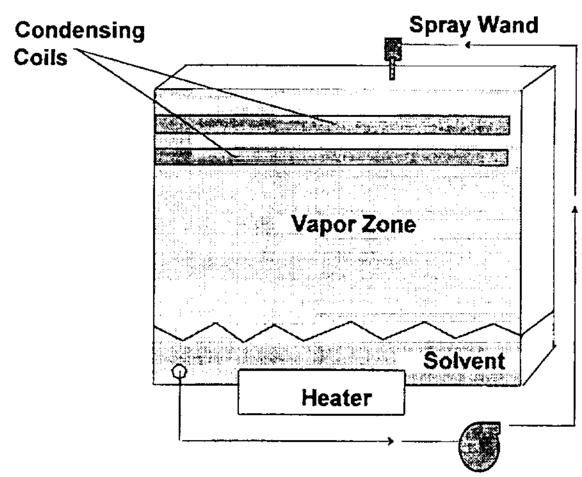
Using new technology, waterbased cleaners are now being developed to replace chlorinated solvents for cleaning metal and composite substrates. These new cleaners, specifically designed for long bath life, are aqueous solutions containing water conditioners, corrosion inhibitors, varying amounts of alkalinity builders and a careful selection of organic surfactants. These ingredients are specially selected for desired foaming, wetting (surface tension) and soil removal properties.

This new technology includes cleaners designed to be self-cleaning. When the cleaner has a greater affinity for the part surface than the soil does, it undercuts the soil. The soil is then released from the part surface. Light oils float while heavier soils such as chlorinated paraffins and particulates settle to the bottom. This way, the cleaning bath can be skimmed and filtered to remove both light and heavy soils. Cleaner concentrate is then added as required to maintain recommended parameters and cleaning continues. Only the contaminants skimmed or filtered from the bath need be hauled away as waste; the liquid can be recycled indefinitely. Shop dirts, cutting oils, fingerprints, grease, carbon, low-melt waxes and road soils can all be readily removed with the new aqueous cleaners. Additionally, by adding heat and/or some mechanical action, these aqueous cleaners can also be used to remove petrolatums and high-melt waxes.

In-Use Comparisons

Cleaning tests conducted on a wide variety of soils shows comparable cleaning efficiency with aqueous chemistry and chlorinated solvents. Every hydrocarbon solvent tested dissolved the soils. Aqueous cleaners either emulsified, saponified or rejected the soils depending on the chemistry of the cleaner and soil involved. Overall, most of the soils tested were removed by one or more aqueous cleaner within the ten minute time frame typical for vapor degreasing.

FIGURE 1.
Traditional Vapor Degreaser



Chlorinated solvents did not remove ink, solder paste and candle wax from metal or composite substrates. Mechanical action was required to remove these soils with aqueous chemistry.

Extraction with boiling water and/or hydrocarbon solvents has shown improved cleaning efficiency with aqueous technology versus TCA when measured by ion chromatography, ICP and FTIR methods. Surface examination using X-Ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) verify these findings.

XPS showed no evidence of offgassing[5] on parts cleaned with aqueous cleaners when exposed to a vacuum at 10^{-8} TORR on either rinsed or unrinsed parts. Rinsing does, however, enhance the aesthetics of the part.

Aqueous cleaners are also used to clean composite surfaces prior to bonding. Bond strength can be measured by Lap Shear Testing. In one study[6], the TCA control had 778 psi Shear Strength versus an aqueous alkaline cleaner with 1239 psi. Other tests used to qualify bonding performance include Double Plate Tensile (DPT) and Peel Tests.

It is a well know fact[7] that many composite materials absorb water during fabrication, therefore offgassing can occur for prolonged periods of time depending on the vent path, amount of water absorbed and temperature of the material. The manufacturer of sensitive parts must determine whether exposure to aqueous environments can be tolerated.

Applying the Findings

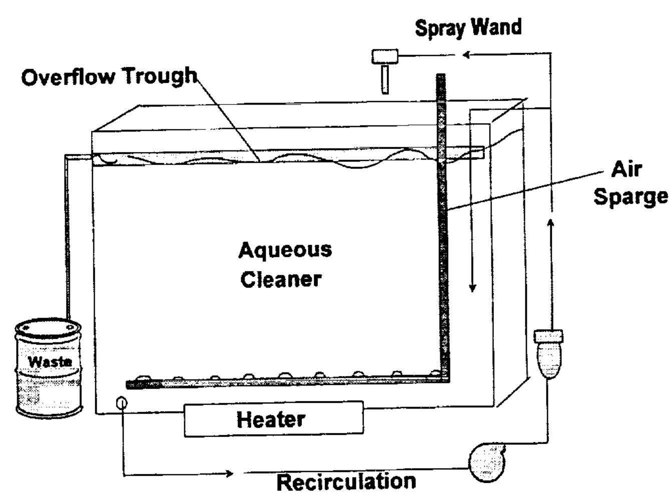
Since these waterbased cleaners have little or no volatile components, with the exception of water, cleaning cannot take place in the vapor phase. Instead, the parts must be immersed in, or sprayed with, the cleaner. Though parts are wet after processing, they can easily be dried with heat, forced air or other means appropriate to the substrate and configuration involved.

Keeping environmental regulations in mind, the manufacturer should select cleaning products that remove the majority of soils at a concentration, temperature and time frame compatible with production needs. To minimize waste, the cleaner selected should have a long or indefinite tank life. Ideally the bath should be filtered periodically to remove contaminants and deionized water should be used for makeup to prevent the buildup of water solids in the bath. Cascading rinses should be used whenever possible with the freshest water in the final stage. Attempts should be made to match the cascade rate to the evaporative loss due to heat. Once again, since the bath need not be dumped, waste is minimized. This in turn translates into reduced costs to the environment and to the company.

Field Testing

Aqueous cleaners have already replaced vapor degreasers in many industries. Making the change has enabled users to eliminate process stages and reduce waste significantly-- in some cases up to 80 percent. Modification of existing equipment as shown in Figures 1 and 2, enables users to convert to aqueous technology without major capital equipment expense.

FIGURE 2.
Modified Vapor Degreaser



A major aerospace manufacturer successfully replaced 1,1,1-trichloroethane with reduced capital expenditures.[7] With slight modifications, the existing vapor degreaser was converted to an 18,000 gallon aqueous immersion bath. The chiller coils were disconnected, the fluid level was raised to allow immersion of parts, and fluid recirculation pumps were added to facilitate agitation. Skimming and filtration were also added to facilitate removal of contaminants. Tank life to date is over three years.

A major manufacturer of flight and non-flight engines has also converted to aqueous technology for the removal of EDM Oil from turbine blades. Five vapor degreaser units have been modified for use with aqueous technology, thus avoiding major capital equipment expenditures.

The subcontractor for a global manufacturer of high tech audio and visual equipment is in the process of converting an existing vapor degreaser to an aqueous spray system. A fine deionized rinse spray over the tank will enhance part aesthetics without requiring a separate rinse tank. The rinse volume will match evaporative loss to minimize bleed-off requirements. The aqueous product selected was custom formulated to meet this customer's potassium and sodium limitations.

The military and automotive industries also have or are in the process of converting existing equipment to aqueous immersion systems for cleaning a wide variety of metal and composite components. One military facility has documented the cost to convert a vapor degreaser at approximately $5000 including all stainless and PVC parts and labor.

In each of the above case histories, tank life has or could have been extended by fluid filtration. Media filters, centrifuges and skimmers all work well in removing contaminants from aqueous cleaning baths.

In addition to the above applications, aqueous cleaners are successfully being used to clean in-flight airplane components, printed wiring assemblies, advanced composites, fasteners, communications components, computer systems and hydraulic systems in the United States and world wide.

New Technology for the Future

Many industries are faced with the challenge of finding new technologies to reduce hazardous chemicals, thus reducing the amount of hazardous wastes generated. Industry must share responsibility with courts and governments around the world for a cleaner, safer environment.

With the new waterbased cleaners, waste minimization is real and obtainable today without loss of cleaning effectiveness. In addition, these aqueous cleaners can be recycled to save on product and disposal costs.

References

[1] Freon is a registered trade name of Dupont

[2] Quitmeyer, J.A., " Aqueous Cleaners Challenge Chlorinated Solvents", *Pollution Engineering,* December, 1991.

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[4] Johnson, J.C., "Vapor Degreasing," *Metal Finishing Guidebook Directory 1987,* Metals and Plastics Publications, Inc., Hackensack, NJ, 1987, p. 103.

[5] Dauphin, J., Dunn, B.D., Judd, M.D., Levadow, F., " AEROSPACE...Materials for Space Application", *Metals and Materials,* July 1991, p. 430.

[6] Harrison, A.C., Marlow, M.E., and Levi, L.D. , *Evaluation of Environmentally Acceptable Cleaners As Replacements for Methyl Ethyl Ketone and 1,1,1-Trichloroethane in Solid Rocket Motor Production and Maintenance Applications,* Aerojet Propulsion Division, Sacramento, CA, July 1992.

[7] Hanson, P.A., *Operational Strategies for Contamination Control of Composite Materials,* Science Applications International Corp., Glendora, CA 91740.

[8] Quitmeyer, J.A., *Modification of Vapor Degreasing Equipment For Aqueous Cleaner Applications,* W.R.Grace & Co.-Conn., Lexington, MA 02173, November 1993.