Fact Sheet

ENVIRONMENTAL SERVICES DIVISION

State of Michigan • Departments of Commerce and Natural Resources

AQUEOUS AND SEMI-AQUEOUS CLEANERS

INTRODUCTION

The traditional way to clean an oily part was to dip it in a solvent or suspend it in solvent vapors. It was fast and effective. Today, however, the liabilities associated with worker safety and management of hazardous wastes and restrictions on production of some chlorinated solvents are motivating businesses to find alternatives to solvents in their cleaning processes. Aqueous and semi-aqueous cleaners are being advertised by their manufacturers as reliable substitutes for solvents in many different cleaning applications. Businesses have many questions regarding these substitutes. Are they effective in cleaning? What waste streams do they produce and how are they treated? Are they friendly to the environment and workers that use them? The purpose of this fact sheet is to help in determining if these cleaners can meet the needs and expectations of your particular requirements.

CONTENTS

P.O. BOX 30004
LANSING, MICHIGAN 48909
(517) 335-1178 • 1-80
FAX: (517) 335-4729

SMALL BUSINESS CLEAN AIR ASSISTANCE

IDENTIFY THE NEEDS OF YOUR CLEANING SYSTEM

Switching cleaners is not as easy as it may sound. There are many variables that affect cleaning. Before evaluating alternative cleaners, assess the cleaning process needs. A check list of factors that affect the selection of a cleaner and its method of application follows.

What Types of Soil are to be Removed?

The first step in assessing cleaning needs is to identify the soils that need removal. The composition of soils to be removed is an important variable in cleaner formulation. If the manufacturing process and storage and handling conditions of the part are known, the type of soil that the part has been exposed to can be predicted. For example, if the parts have gone through machining operations, oils and greases used for lubrication, cutting, quenching and rust prevention must be removed. Consider the removal of solder flux residues when cleaning electronic components. Parts exiting metal polishing and buffing operations are contaminated with waxes and abrasives.

As can be seen in Table 1, there are a variety of soils. Physical properties of soil include its state (liquid or solid), viscosity, polarity and melting point. Solid particles (metal chips, abrasive grains, pigments, carbon smut and shop dirt) are usually held on the part by oils and greases or static electricity. Because of the large surface area of the tiny particles, they hold on to the part with great tenacity. Liquid soils, such as lubricants and oils, which are left on parts for a long time or heated, can polymerize to form tough hard films. Also, soils with high viscosity and melting points are generally more difficult to remove.

The polarity of soils will affect the type of cleaner selected. Polar or ionic soils are positively or negatively charged particles due to the loss or gain of electrons. Most inorganic soils (substances that are not compounds of carbon) are polar, whereas most organic soils (substances that are compounds of carbon) are non-polar. Water is a polar substance. Most hydrocarbon liquids, with the exception of alcohols, are non-polar. The importance of polarity of both the soil and the cleaner will be addressed later, in the discussion of the cleaning mechanism of solvency.

Substrate

Zinc and aluminum alloys, because of their sensitivity to alkaline cleaners--which are corrosive--will require different cleaners than ferrous alloys. Aqueous cleaners for nonferrous alloys will be formulated with

TABLE 1

SOILS	
SOIL TYPE	**OPERATIONS**
Oily soils: animal, vegetable and petroleum oils	Metal cutting, metal forming and rust protection.
Semi-solid soils: greases, soaps, abrasives and waxes	Buffing and polishing
Solid soils: carbonaceous films, metal oxides and shop dirt	Heat treating and storage

inhibitors that prevent the alkalies from attacking the sensitive metals. The inhibitors deposit a thin protective layer on the metals as soon as the contaminants are removed. The majority of aqueous and semi-aqueous cleaners are compatible with most metals and plastics.

Part Size and Configuration

Part configuration, size, weight, porosity, and quantity will not influence cleaner chemistry, but will determine the method of cleaning and parts handling. Parts with rough surfaces, overlapping joints, blind holes and tubing must be positioned to avoid corrosion from the carry out of cleaner. Very large castings may affect temperature of the cleaning bath and more heat must be added to the cleaning bath to maintain cleaning efficiencies.

What is the Acceptable Level of Cleanliness?

The level of cleanliness is dependent upon performance requirements of the part. Parts going on to a painting or electroplating process will have to be "cleaner" than if the parts were headed to a machining operation. Many standard tests can be used to determine if the acceptable level of cleanliness is being met. They range from visual inspection to elaborate laboratory testing. A simple and reliable procedure is the water-break test. A surface is considered clean if it can hold a complete film of water on the surface of the work after a 30 second drainage period. If a water-break appears, the surface is not clean.

Other Considerations

Source Reduction: One way of reducing costs and increasing the potential of making a successful conversion to a new cleaning system is to reduce the amount of contamination on the parts. Once the source of the contaminants is identified, modifications can be made that will reduce or eliminate the need for cleaning. If the soils are:

- received in raw materials, talk to suppliersabout what they can do to reduce the contamination;
- produced in general machining operations, minimize the number of different coolants and/or lubricants used;
- produced in subassembly, find ways to reduce handling; or
- produced during storage, reduce moisture.

Potential Impacts: In order to successfully make the switch to your new cleaning system and reduce the impact to other operations, consider the following questions:

What are the waste streams that will be created by the new system and how are they to be managed?

What new operating skills or equipment maintenance will be needed? Process controls for aqueous and semi-aqueous cleaning systems are greater than those needed for solvent cleaning systems.

How will the modification affect product quality and operating rates?

What are the capital and operating costs? Energy requirements for aqueous cleaning systems are greater than solvent vapor degreasing.

And finally, have any substitutions been attempted in the past? What worked? What did not work and why?

EVALUATION OF AQUEOUS AND SEMI-AQUEOUS CLEANERS

Cleaning Step

Unlike solvent cleaning, which occurs in one step, aqueous and semi-aqueous cleaning invclves three steps: cleaning, rinsing and drying. The cleaning phase in aqueous and semi-aqueous systems differ; however, the rinsing and drying steps for aqueous and semi-aqueous cleaning systems are nearly identical.

Cleaning Mechanisms

A discussion of aqueous and semi-aqueous cleaning should not proceed without some understanding of the following four basic cleaning mechanisms:

Mechanical action - This is the lifting of contaminants by physical agitation, i.e., wiping, brushing, spraying or abrading.

Chemical reaction - There are two basic chemical reactions that can occur in aqueous cleaning: saponification and sequestration. Saponification occurs when the alkalinity of the aqueous cleaner "splits up" fatty acids, a contaminant, to form water soluble soaps that can be easily removed. Sequestering agents (polyphosphate salts of sodium) or chelating agents (ethylenediamine tetracetic acid) are added to cleaner formulations to "tie-up" or sequester the calcium and magnesium ions in hard water so that they do not interfere with cleaning. The hard water ions are formed into ringed structures that are water soluble and chemically inactive. If not sequestered, the ions will react with soap to form scum.

Solvency - Soils (or solutes) will dissolve in a solvent forming a uniformly dispersed mixture or solution. Water, being a polar substance, is the solvent for many polar (or ionic) soils. Hydrocarbons, being non-polar, are the solvents for non-polar or organic soils. Solubility is the term commonly used to describe the ability of solids to dissolve in

SURFACTANTS

Surfactants, also known as surface-active agents, are composed of molecules that have two dissimilar parts resembling a tadpole. The tail end is made up of a chain of carbon atoms and is soluble in oil or, in other words, attracted to dirt, oil and grease. The head is ionic and is attracted to water. The nonpolar hydrocarbon end stays in the oil and the polar, ionic end is in the water. Because of this antagonistic action, surfactants like to concentrate at surfaces or interfaces.

As the number of carbon atoms included in the chains increase, the surfactant molecules' oil attractive properties increase and their water attractive properties diminish. Surfactants with relatively high oil-attractive properties are called **emulsifiers.** Emulsifiers coat oil and grease, which forms an emulsion. The emulsifiers suspend the organic soils and grease and other water immiscible soils in solution and prevent redeposition. Surfactants with relatively low oil-attractive properties are called **wetting agents.** Wetting agents increase the penetration of the cleaner on the surface or soil by reducing surface tension. **Detergents** possess oil-attractive properties between those of wetting agents and emulsifiers. Detergents lift soil from the surface of the part by replacing it with a surfactant, which has a greater affinity for the soil.

Detergents or synthetic surfactants are made from alcohols or petroleum derived fractions. Soap is an organic surfactant formed by the reaction of fatty acids (derived from natural fats, such as tallow, fish oil and vegetable oils) and caustic soda.

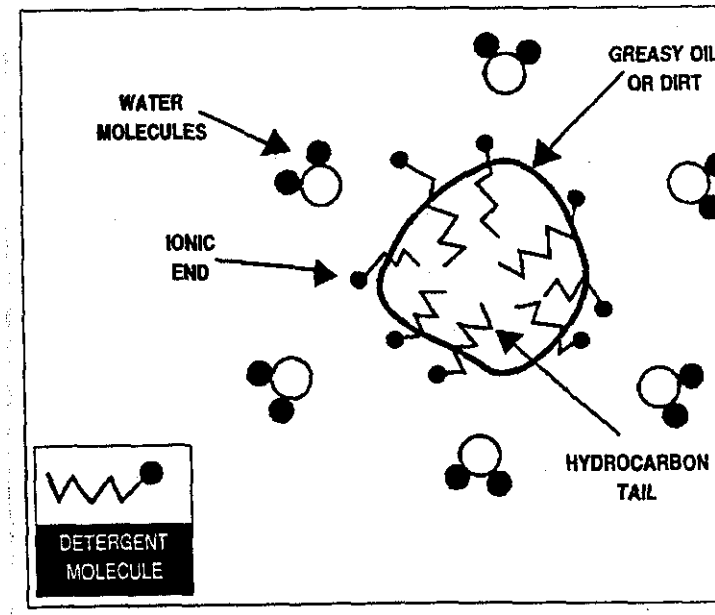


Illustration of an emulsified drop of oil in water with detergent a emulsifier. The nonpolar hydrocarbon tail of the detergent mole is in the oil, and the ionic end is in the water.

liquids and miscibility is the ability of a liquid to dissolve in another liquid.

Detergency - This is the lifting of soil from a surface by displacing it with surfactants that have a greater affinity for the soil than the surface. The surfactants also provide for the dispersion of the contaminates, which is necessary to prevent recontamination.

Aqueous Cleaners

•How Do They Work?

Aqueous cleaners are categorized by pH level. Cleaners with a low pH (2 to 6) are acidic and those with a pH of 6 to 8.5 are considered neutral. Cleaners that have a high pH (8.5 to 13) are considered basic or alkaline. Acidic cleaners contain excess hydrogen ions (H+) and alkaline cleaners contain excess hydroxide ions (OH-). Acid cleaners are primarily used in removing oxidation scale and rust. Acid cleaners contain mineral acids (nitric, phosphoric, sulfuric, and hydrofluoric); chromic acid or organic acids (acetic and oxalic); plus chelating agents, detergents and small amounts of water-miscible agents.

Aqueous cleaners, because they are water based, are most effective on polar, inorganic based soils; however, a variety of additives enhance the cleaners to provide for the removal of organic soils as well. In aqueous cleaning, a combination of the cleaning mechanisms are employed: mechanical action, chemical action and detergency.

Because their performance can be affected by concentration, temperature and formulation, aqueous cleaners can be used in a variety of applications. Alkaline cleaners are formulated to be either broad spectrum or precisely applicable. Broad spectrum cleaners remove a variety of soils while precisely applicable cleaners are highly effective for a specific soil and not effective for many other soils.

•Composition

Aqueous cleaners contain several chemical components each having a distinct function and effect on the way soil is removed.

Alkaline Salts - Alkaline salts or alkalinity builders are the major components in alkaline cleaners. They act as buffers that neutralize acidic soils without excess loss of alkalinity and maintain the chemical environment in which other components of the cleaner operate.

Alkaline salts can be categorized by the way they condition or soften water. The two groups of alkaline salts are precipitating and sequestering. Precipitating salts will combine with hard water minerals making them insoluble. Sequestering salts will tie up minerals and soils and hold them in suspension, making them soluble. Examples of some common cleaners are found in Table 2.

TABLE 2

TYPICAL ALKALINE CLEANERS	
PRECIPITATING TYPE	**SEQUESTERING TYPE**
Caustic soda (pH 14.0)	Sodium tripolyphosphate (pH 10.5)
Soda ash (pH 11.5)	Tetrasodium pyrophosphate (pH 10.0)
Trisodium phosphate (pH 12.0)	Sodium hexametaphosphate (pH 8.0)
Sodium metasilicate (pH 12.5)	
Sodium orthosilicate (pH 13.5)	

Footnote: *Scislowski, Stan "Cleaning Basics: Alkaline Cleaners" Metal Finishing.*

Sequestering type alkaline cleaners are more effective in preventing the buildup of hard water scale on tanks and pumps. They are effective in "peptizing" or holding soils in suspension, which prevents them from redepositing on the part. Phosphates are the best overall builders, however, their discharge is subject to regulation.

Precipitating alkaline cleaners have higher alkalinity and, therefore, higher pH. Silicates are used in cleaning non-ferrous metals such as zinc, brass and aluminum because they inhibit the corrosive action of the alkalinity. One disadvantage in using the precipitating type cleaners is their poor rinsibility. Hard water minerals that precipitate out cling to the sides and bottom of the tank. This contributes to the redeposition of soil onto the part.

Surfactants - Surfactants can penetrate, displace and/or emulsify soil. (See Page 4). They are classified as anionic, cationic or non-ionic. Anionic and cationic surfactants are used in immersion cleaning. A non-ionic surfactant should be used if aqueous spray cleaning or agitation is used in order to minimize foaming. Some of the commonly used anionic surfactants are alkyl benzene sulfonates and naphthalene sulfonates. Most surfactants are biodegradable. Soaps (organic surfactants) are destroyed in acid and perform better in alkaline conditions. The optimum alkalinity for soaps is 10.5.

Saponifiers - Saponifiers are alkaline cleaners that react chemically with insoluble animal fats and vegetable oils to form water soluble soaps. Saponified soils float to the top of the tank and are removed by skimming. Many buffing compounds contain insoluble fats and fatty acids.

Rustproofing Inhibitors - Compounds such as urea type inhibitors are added to the cleaners or used in the final rinse water to protect the part from rusting.

•*Methods of Application*

The cleaning phase in an aqueous cleaning system occurs in one step. The contaminan are removed from the parts in the tank containing the cleaner. The parts leaving th cleaning tank are coated with a water/deterg film containing minor amounts of contamin Cleaning cycle times for aqueous cleaning i industrial applications range from 2 to 30 minutes.

The method of cleaning is dependent on production rates, available space, and size a shape of part. The basic cleaning methods a immersion (dipping or soaking) with or wit agitation, spraying or by a combination of immersion and spraying. The different type cleaning machines are found in Table 3.

Immersion - Immersion of parts into a clear tank is simple, efficient and is the most wid practiced aqueous cleaning method. Tanks accommodate parts of unusual shape and a not costly to set up.

Installations may vary from single unheatec tanks to multistage systems equipped with and agitation. Aqueous cleaners need to be heated, especially when removing inks, wa or solder pastes. The normal temperature o cleaner is in the range of 160°-200° F. The speed of chemical reactions in cleaning do with each 20° F rise in temperature. Heat i provided by steam coils, plate coils, direct burners or immersion electric heaters. Lov temperature cleaners, which operate at a temperature range of 70° - 120° F, are a litt more expensive to purchase; however, they greatly reduce energy costs and still provid good cleaning.

Workpieces and/or cleaning solution are agitated to improve cleaning efficiency an reduce cycle times, temperature requireme and the formation of air pockets. Agitatio immersion cleaning includes workpiece movement, such as withdrawal and reimmersion, pump agitation and ultrason

TABLE 3

TYPES OF CLEANING EQUIPMENT		
MACHINE	VOLUME OF PARTS	TYPE OF PARTS
Flat belt	Medium-High	Parts that drain easily
Rotary drum	Medium-High	Small intricate parts and irregular shapes that trap fluids
Monorail	Low-High	Large sheets
Turntable	Low	Parts requiring special positioning for draining
Cabinet	Low	Medium to large sized parts of any shape

Pumps should be used for solution agitation rather than blowers or compressors. Providing agitation through air pressure movement can introduce contaminants into the cleaning bath and can create excessive foaming. Ultrasonics create cavitation (bubbles) at the cleaning surface using high frequency vibrations. As the bubbles form and collapse, they create a scrubbing action that cleans the surfaces of the part including blind holes and very small cracks and crevices.

Quite often, existing equipment such as vapor degreasers can be converted to the use of aqueous cleaners. Under the direction of some manufacturers of aqueous products, the changes can be implemented quite easily and economically.

Spray Cleaning - Spray cleaning involves the impingement of cleaning solution upon the workpiece to remove soil. It is typically used for conveyorized part handling systems and high production rates. Spray washers consist of a pump to pressurize the solution, a reservoir tank, connecting piping, spray nozzles and a means for moving workpieces through the nozzles and cleaning solution.

For small parts, cabinet or carousel machines provide the simplest method of spray cleaning. Inside the machines, a drum or worktable rotates or reciprocates so that surfaces of all the workpieces can be exposed to the spray.

Large flat parts are typically carried through washer tunnels or monorail washers by conveyor.

The spraying action provides a high level of impact and agitation. Spray pattern, volume, pressure and angle of spray can have an effect on cleaning efficiency. The higher the spray pressure, the greater the mechanical cleaning action. Spray pressure can vary from 2 to 2000 psi. The design of the spray nozzle is critical because it provides the high impact, flat spray pattern and required flow rates. Increasing the spraying pressure results in higher impact velocities and flow rates with smaller drop sizes.

While it is difficult to maintain the cleaner at a high temperature because of heat loss during recirculation and spraying, it is still desirable to keep the cleaner in the temperature range of 130°-160° F. Cleaners used in spray washers require non-ionic surfactants to prevent foaming.

Spray cleaning has some advantages over immersion in that it takes less time to clean and a lower concentration of cleaner is used. The amount of cleaner can be as low as 10% of that required for immersion cleaning. One disadvantage, however, is that the capital costs for spray cleaning is greater than for immersion cleaning.

•*Safety*

Aqueous cleaners are nonflammable. Because of their alkalinity, aqueous cleaners have an ability to extract oils out of skin. Workers should wear rubber gloves, aprons and face shields to prevent contact with skin. Handling and safety requirements identified in the cleaner's Material Safety Data Sheet (MSDS) should be followed without exception.

•*Cost*

Aqueous cleaners are available in concentrated liquids and powders. Liquids cost $6 to $10 per gallon when purchased in drum quantities. In most applications, the cleaner is diluted with water within the following range; 1 part cleaner to 3 parts water (1:3) to 1 part cleaner to 10 parts water (1:10). In an effort to reduce waste disposal costs, some manufacturers are packaging liquid cleaners in recyclable 250 gallon containers.

•*Recovery and Disposal*

Recovery - In parts cleaning systems, cleaning power and contamination level are inversely proportional: By continually removing contaminants from the cleaner, the cleaning ability is maintained and thus the cleaner can be recycled indefinitely.

Increasing the longevity of the cleaner starts with selecting the proper cleaner formulation. Purchase a cleaner that provides good separation of the soils from the cleaner. New oil-displacing cleaners, or cleaners that are good detergents but poor emulsifiers, allow the separation to occur. These cleaners will allow oily soils and saponified soils to float to the surface where they can be skimmed off. The heavy soils settle to the bottom where they can be filtered off and collected as a sludge.

Cleaners containing emulsifiers can form one of two types of emulsions: permanent or quick breaking. Permanent emulsions keep the oil in suspension indefinitely, and quick break emulsions are temperature sensitive, which allows rapid separation of the water and orga contaminant.

In cleaners containing quick break emulsions oils are put into suspension at operating temperatures of 140° F and above. Upon cooling to 85° F, the oil will separate from th water and cleaning component mixture, form two layers. The organic oil layer can be disposed and the water/cleaning component layer can be reused. Cleaners with quick bre emulsifiers cost more but have a longer life.

In addition to choosing the right cleaner, the are various processes that can remove contaminants so that the cleaner and rinse waters can be can be continuously recirculat Free oils, emulsified oils, and suspended soi and metals are the contaminants that should removed continuously or periodically from t aqueous cleaner bath and rinse water.

A continuous small stream of cleaner can be directed to a concentration or clarifier tank located adjacent to the cleaning bath tank (s Figure 1 on page 9). The concentration tanl provides for the separation of solids and liq by gravity and floatation. The free oils that float to the top of the tank can be removed b oil skimming devices or absorbent mats tha pick up petroleum based fluids but repel wa and product. The contaminants heavy enou settle out can be passed through a bag filter filter press and removed as a sludge.

Microfiltration membranes, which have a p size of greater than 0.2 microns, remove di and contaminants (concentrate) from the cl bath while allowing the cleaner and water (permeate) to pass on through. The cleane water are returned to the cleaning bath tanl Ultrafiltration membranes, which have a p size between 0.001 and 0.1 microns, can a remove contaminants from the rinse water

In addition to membrane technology, cold vaporization, ion exchange encapsulation ..

chemical treatment systems can be used to purify cleaners and rinses so that they can be reused.

Disposal - When it comes to disposing a cleaner bath, there are a few options:

- discharge to a holding tank from which the waste is subsequently pumped and hauled by a licensed hauler for appropriate disposal at an approved facility;
- discharge to surface waters or groundwater if permitted or exempted by the Michigan Department of Natural Resources (MDNR) under the Michigan Water Resources Commission Act (Act 245 of 1929); or
- discharge to a Publicly-Owned Treatment Works (POTW) with the approval of the POTW.

Approval for discharging to a POTW, surface water or groundwater may be contingent upon pretreating the waste to remove the oils and grease and adjusting the pH and removing organic matter and dissolved metals. Refer to the "Environmental Regulatory Considerations" section of this fact sheet for more details.

Even though the cost of equipment to recover and treat aqueous cleaners can be expensive, the same equipment could be used on other waste streams generated at your business such as machining coolants and mop water.

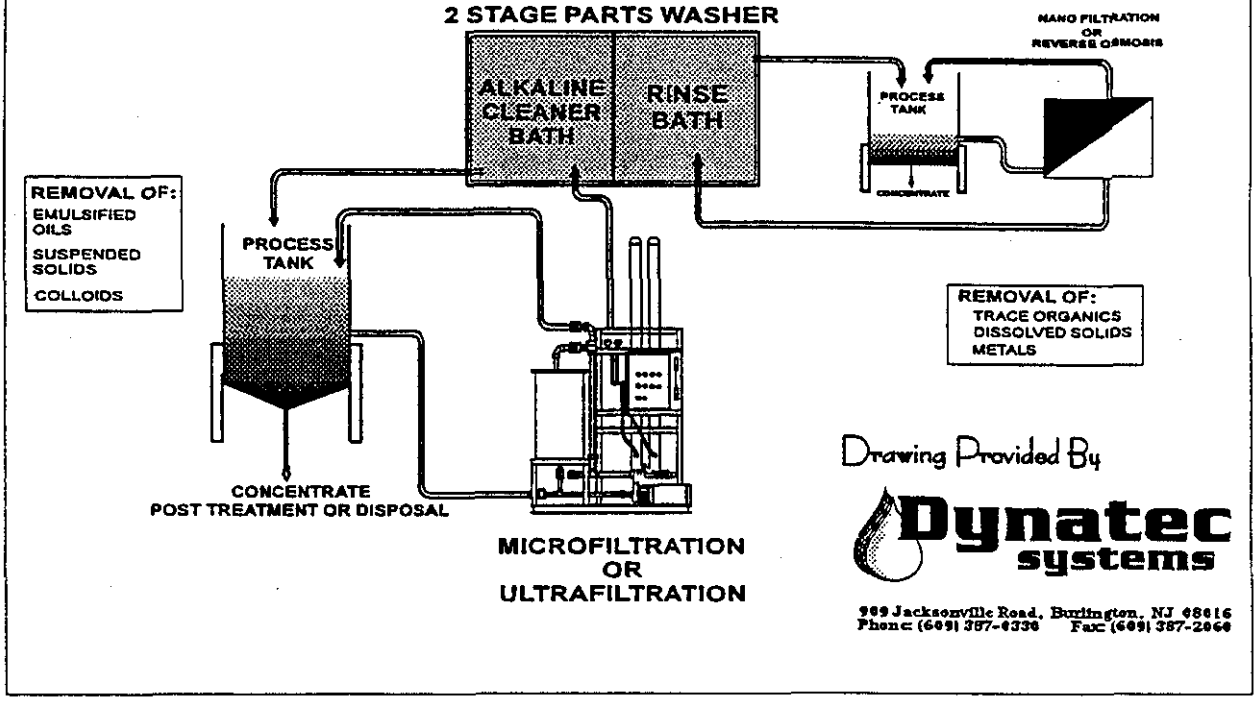
Semi-Aqueous Cleaners

•How do They Work?

Semi-aqueous cleaners, also known as emulsion cleaners, are nonchlorinated hydrocarbons dispersed in water with or without the aid of emulsifiers. They, therefore, have the cleaning properties of solvency and detergency.

Whereas the cleaning phase for aqueous cleaners occurs in one step, the cleaning phase for semi-aqueous cleaners generally occurs in two steps. The soil and contaminants are dissolved in the primary tank containing the cleaner. In the secondary tank, the soil/cleaner

FIGURE 1.



mixture is rinsed off the part with water. Like aqueous cleaning, the parts then proceed through the rinsing and drying phases.

Due to their solvency properties, semi-aqueous cleaners are effective in removing heavy greases and waxes. They traditionally have been used as an in-process cleaner, removing the bulk of the soils so that further manufacturing can be conducted without difficulty.

•*Composition*

There are two basic components of semi-aqueous cleaners, and they are categorized by their ability to mix with water. Water immiscible components include:

Terpenes - These are natural hydrocarbons derived from plants. d-Limonene is extracted from the rinds of lemons and oranges. Pinene is extracted from the bark of pine trees.

Esters - Aliphatic monobasic esters and dibasic esters are used in semi-aqueous cleaners.

Water miscible components of semi-aqueous cleaners include:

Glycol ethers - There are two common kinds of glycol ethers: e and p series. The p-series are typically used in cleaning formulations because they are safe for personal contact and not regulated under Section 313 of the Emergency Planning and Community Right-to-Know Act.

Ketones - Commonly used ketones in cleaning are acetone and methyl ethyl ketone.

Alcohols - Commonly used alcohols used in cleaning are ethanol and isopropyl alcohol.

Amines - N-methyl-2-pyrrolidone (NMP) is an amine that is used in paint strippers as a replacement for methylene chloride.

Surfactants - See Page 4 for definition.

Alkaline Builders - See Page 6 for definition.

•*Methods of Application*

Immersion is the most common method of contacting the part with the semi-aqueous cleaner. Because of the relatively low flash point of organic solvents, terpenes in particul there are limitations to the degree of heating agitation applied to the cleaning tank.

To avoid ignition of solvent vapors, it is recommended that a minimum of 30° F is maintained between the operating temperatur of the cleaner and its flash point. Terpenes, which have a flash point in the range of 115° 120° F, should not be heated above 90° F unl diluted with water. Glycol ethers and NMP have flash points of 142° and 204° F, respectively.

Although agitation increases cleaning efficie and emulsion stability, care must be taken to avoid creating mists of concentrated semi-aqueous cleaners. These mists can be ignited room temperature.

•*Safety*

In addition to the flammability concerns identified above, there are some worker safet concerns associated with terpene cleaners. Since they are derived from plants, they can have an odor that is bothersome to some workers. Ventilation systems may have to be provided in areas where the cleaners are used

Toxicity studies on terpenes as well as other cleaner components are being conducted. According to an EPA report entitled Aqueou and Terpene Cleaning Interim Report, "... aqueous and terpene cleaners can be used in manner safe to workers, consumers, and the general population given appropriate technological changes and exposure control practices."

Since the cleaners are moderate skin irritants solvent resistant gloves and aprons and eye protection should be worn where exposure is likely. Handling and safety requirements identified in the cleaner's Material Safety Da

Sheet (MSDS) should be followed without exception.

•*Cost*

Terpenes, esters and glycol ethers are priced at $10 to $18 per gallon when purchased in drum quantities. NMP's cost is $25 to $30 per gallon.

•*Recovery and Disposal*

Recovery - Since oils tend to dissolve in semi-aqueous cleaners, skimmers and coalescers are not as effective in the removal of these contaminants. Concentrated semi-aqueous cleaner baths are not reclaimable. Contaminants dissolve and become locked up in the hydrocarbon solvent making separation of the dirt from the cleaner difficult. Once they become contaminated, the cleaning bath must be disposed. The rinse waters of the semi-aqueous cleaning system can be recycled by microfiltration membranes or ion exchange.

Disposal - The disposal options for semi-aqueous cleaning baths diluted with water are the same as those identified for aqueous cleaning baths. Concentrated semi-aqueous cleaners, because of their high BTU value, may be picked up by a licensed hauler and taken to approved facilities that process wastes into a fuel that is burned for energy recovery.

Rinsing Step

To obtain the required level of cleanliness, parts exiting the aqueous or semi-aqueous cleaning bath should be rinsed. Rinsing is necessary to remove the residual layer of contaminants and cleaner. Not all cleaners rinse the same. Semi-aqueous cleaner residue is more difficult to remove than aqueous cleaners. The level of rinsing ranges from simple immersion or spray using tap water to multiple rinse tanks using deionized water.

To minimize water usage, a counterflow rinsing system should be used. In a two tank counterflow system, water in the final or secondary rinse tank is used to replenish the initial or primary rinse tank.

Heat, agitation and chemical additions will increase the effectiveness of rinsing. Rinse water should be warm as opposed to hot or cold. Hot water may set some of the residues on the part or form oxide films. Temperature also affects the surface tension of water. More droplets will cling to parts rinsed with cold water than with warm water. Ultrasonics or pumps provide the mechanical action necessary to increase rinsing efficiency. Consideration should be given to using deionized water for rinsing parts, which eliminates the spotting caused by the salts found in hard water. Adding isopropyl alcohol to the rinse water improves rinsing by reducing the surface tension of the water.

Drying Step

Unlike solvent vapor degreasing, in which parts come out dry, aqueous and semi-aqueous cleaned parts are wet. Drying can be accomplished by a variety of methods depending upon part configuration and the speed required. Typical methods of drying include evaporation, mechanical displacement of water or displacement using another fluid.

Evaporation under ambient conditions is slow and can lead to rusting. Evaporation is accelerated by putting the parts in a chamber that circulates heated air. Air knives blow off water from the part with compressed air. It minimizes the deposition of dissolved solids that may remain on the part. Centrifugal drying spins water off. Special protective oils displace water from the part and replace it with a film that prevents corrosion.

ENVIRONMENTAL REGULATORY CONSIDERATIONS

Waste streams generated from aqueous and semi-aqueous parts cleaning systems can include used oils, wastewater (cleaning baths and rinse waters) and even some small

amounts of volatile organic compounds (VOCs). In general, the options for wastewater disposal are: (1) contracting with a hauler to deliver it to a commercial treatment and disposal facility, or (2) pretreating the wastewater on-site prior to discharge to a POTW or other approved receiver. On-site pretreatment may generate sludge, which is another waste stream requiring disposal. The environmental regulatory considerations for all of these waste streams are discussed below.

Used Oils

Used oils that are separated from cleaner solutions by devices such as skimmers and coalescers can be disposed in the same manner as other used oils that may be generated from other production or maintenance processes. If the used oil is recycled, the generator is exempt from the requirements of Michigan's Hazardous Waste Management Act, 1979 PA 64, as amended (Act 64).

If the used oil will be burned for energy recovery, the generator will be subject to the hazardous waste requirements under Act 64. Used oil destined for burning is identified as either on-specification or off-specification. Used oil is considered to be "off-spec" unless laboratory results or other documentation shows that contaminant levels do not exceed specifications. For more information regarding the requirements for this management option, contact your nearest Michigan Department of Natural Resources' (MDNR) district office.

All generators of used oil must comply with the management standards promulgated under special authority of the federal Resource Conservation and Recovery Act (RCRA), Section 3014(a). These standards were issued to control potential risks from recycled used oil and, according to these requirements, a generator must:

- Keep storage tanks and containers in good condition;
- Label storage tanks, "used oil";
- Clean up any used-oil spills or leaks to the environment; and
- Use a transporter with an EPA identification (ID) number when shipping used oil off-site. The transportation of used oil in Michigan is also subject to the requirements of Michigan's Liquid Industrial Act, 1969 PA 136 as amended (Act 136). A contract hauler of liquid industrial waste, regardless of whether or not the material is hazardous, must be licensed and a manifest must accompany the shipment.

Wastewater (Off-site Treatment & Disposal)

Before sending spent cleaners (or liquid industrial waste) to an off-site facility for treatment and disposal, it is the generator's responsibility to determine if the waste is a hazardous waste. There are two categories of hazardous wastes: listed and characteristic. Listed wastes are waste materials listed by name in either Act 64 or the Resource Conservation and Recovery Act (RCRA). Characteristic wastes are wastes that possess any of the characteristics identified in state and federal hazardous waste law. These characteristics include corrosivity, ignitability, reactivity, toxicity and severe toxicity.

If the wastewater is determined to be non-hazardous, it is not regulated under Act 64 or RCRA. However, like used oil, the transportation of the wastewater is subject to Act 136.

If the liquid industrial waste is determined to be a hazardous waste, it is subject to all applicable requirements pursuant to state and federal hazardous waste regulations. This would include transporter licensing and disposal at a licensed hazardous waste treatment, storage or disposal facility (TSDF).

Depending on the hazardous waste characterization and amount of recoverable oils, liquid industrial wastes will typically go to one of three types of facilities.

Used oil processors will treat non-hazardous liquid industrial waste containing recoverable oils in addition to processing used oils. The used oils are separated from the wastewater and are processed for fuel use or non-fuel industrial uses, such as cutting and honing oils. The treated wastewater is discharged to a POTW.

Licensed hazardous waste TSDF facilities will process both non-hazardous and hazardous liquid industrial wastes containing recoverable oils. The used oils are reclaimed and the treated wastewater is discharged to a POTW. A price break is given to non-hazardous liquid industrial wastes.

Licensed hazardous waste TSDF facilities will solidify both non-hazardous and hazardous liquid industrial wastes. The solidified material is landfilled. This disposal option is best suited for wastes that are heavily contaminated and/or have very little BTU value.

Wastewater (On-site Pretreatment)

Businesses must sometimes pre-treat chemical wastes prior to disposal. The level of pretreatment depends upon the quantity and nature of the contaminants and the limitations imposed by the POTW if discharged to a sanitary sewer; the National Pollutant Discharge Elimination System (NPDES) permit if discharged to surface waters; or state groundwater permit if discharged to the groundwater.

There are two types of national pretreatment standards that control pollutants introduced into a POTW: prohibited discharge standards and categorical pretreatment standards. Prohibitive discharge standards are contained in the general pretreatment regulations, which are found in Title 40, Part 403 of the Code of Federal Regulations (40 CFR Part 403). These standards are designed to prevent pass through or interference with the treatment processes at the POTW. Categorical pretreatment standards regulate the level of pollutants discharged to the POTW for specific types of industries. The categorical pretreatment standards appear in 40 CFR Parts 405 through 471.

pH Adjustment - Since aqueous cleaners are alkaline and have a pH ranging between 7 to 12, pH adjustment may be required prior to sanitary discharge. Sulfuric or hydrochloric acid are typically used to lower the pH.

Biodegradable - Many manufacturers claim their aqueous and semi-aqueous cleaners are biodegradable. This can be somewhat misleading because the term biodegradable applies only to the cleaner. It does not apply to the contaminants in the cleaner. Also, some surfactants take too long to break down into the constituent elements to be environmentally acceptable. If the amount of dissolved metals and/or emulsified oils in the waste stream exceeds the POTW, NPDES or groundwater permit discharge limits, they will have to be removed from the waste stream prior to discharge.

Free Oil Removal - Free oils will rise quickly to the surface of a nonagitated tank. Skimmers have either a rope or drum that lifts the oil from the surface of the cleaner and deposits it into a holding tank. Devices such as coalescers and centrifuges will improve the separation of free oil from the cleaner.

Emulsified Oil and Metal Removal - Removing dissolved metals and emulsified oils from aqueous cleaners can be achieved through chemical treatment or membrane separation. The chemical removal of stable oil-water emulsions and dissolved metals occurs in three steps:

(1) a coagulant is added to break the oil-water emulsion and a hydroxide, such as lime, precipitates out the dissolved metals;

(2) a flocculent is added to agglomerate the tiny oil particles and metal precipitate into particles; and

(3) the particles are separated from the clean water through sedimentation and removed. The chemical treatment of wastewater generates sludge, which is typically dewatered prior to disposal.

Reverse osmosis can remove dissolved metal ions from the cleaner solution. Ultrafiltration membranes can remove emulsified oils.

Sludge Removal - Pretreatment of wastewater may result in creation of a sludge. The sludge must be evaluated to determine if it is sufficiently dewatered and if it is a hazardous waste. If the sludge has been determined to be non-hazardous waste, it can be disposed in a sanitary landfill licensed under Michigan's Solid Waste Management Act, 1978 P.A. 641, as amended (Act 641). Liquid waste cannot be landfilled.

Air Contaminants

Michigan's Air Pollution Act, 1965 P.A. 348, as amended (Act 348) regulates sources of air pollution. According to Rule 201, "... a person shall not install...equipment...which may emit an air contaminant unless a permit to install ...is issued."

Aqueous and Diluted Semi-Aqueous Cleaners - Parts washing processes utilizing aqueous cleaners and semi-aqueous cleaners diluted with water could meet one or all of the following permit exemptions.

Rule 281 (d), "the permit system does not apply ... to equipment used for washing or drying materials, where the material itself cannot become an air contaminant, if no volatile organic compounds are used in the process and no fuel is burned."

Rule 285(i)(iii), "the permit system does not apply to ... equipment for surface preparation of metals by use of aqueous solutions, except for acid solutions."

Rule 285(o)(iv), "the permit system does not apply to ...equipment used for ... cleaning ... the process emissions are only released into general in-plant environment."

Undiluted Semi-Aqueous Cleaners - Semi-aqueous cleaners used in concentrated form could meet the permit exemption identified i Rule 285(o)(iv).

Although aqueous and certain semi-aqueous cleaning systems are exempt from permitting requirements, all cleaners are still subject to Parts 6 and 7 of the Act 348 rules, which regulate the usage of VOCs in existing and n cold cleaners, respectively. The rule require that the equipment meet various design crite and good operating practices to minimize the release of VOCs.

For more information concerning:

- The disposal of solid and hazardous wastes and transportation of liquid industrial wastes, contac Waste Management Division in your local MI district office.
- The NPDES requirements, contact the Surface Wa Quality Division in your local MDNR district offic
- Discharges to sanitary sewers, contact your PO
- The regulation of air contaminants, contact the Quality Division in your local MDNR district offic
- Suppliers of semi-aqueous cleaners and aque parts washing equipment, contact the Environme Services Division, Departments of Commerce Natural Resources.

Michigan Department of Natural Resources Environmental Protection District Offices

Marquette	..(906) 228-656
Cadillac	.....(616) 775-972
Gaylord	.....(517) 732-354
Grayling	.....(517) 348-637
Bay City	.....(517) 684-914
Grand Rapids	.....(616) 456-507
Shiawassee	.....(517) 625-460
Plainwell	.....(616) 685-988
Jackson	.....(517) 780-790
Livonia	.....(313) 953-024

REFERENCES

- Chiarella, William J., "Alternative Chemicals and Processes in Metal Cleaning," Metal Finishing, Vol. 88, No. 12, Dec. 1990, pp.21-23.
- Environmental Restoration and Waste Management and the U.S. Air Force Engineering and Services Center, Solvent Substitution, [A Compendium of Papers From The First Annual International Workshop on Solvent Substitution], Phoenix: USDOE, December 1990, DE-AC07-76ID01570.
- Huddle, Richard F., "Fact Finding First -- How to Plan the Best Possible Parts-Cleaning System," Products Finishing, March 1990, pp.70-75.
- Innes, William P., "Metal Cleaning," Metal Finishing -- Guidebook and Directory Issue, '90, Vol. 88, No. 1A, Mid-January, 1990, pp.106-124.
- Jansen, George and Jan Tervoort, "New Concept for Alkaline Cleaning -- Low Temperatures and Infinite Bath Life," Metal Finishing, April 1985, pp.63-67.
- Mohler, J. B., "Alkaline Cleaning for Electroplating," Metal Finishing, Sept. 1984, pp.49-52.
- Obrzut, John J., "Metal Cleaning: The Key Element to Better Finishes," Iron Age, 7 June 1982, pp.57-62.
- Overton, Cecil, "Cleaning With Kindness," Products Finishing, April 1992, pp.98-102.
- Polhamus, Robert L., "Precision Cleaning of Metal Parts Without Solvents," Metal Finishing, September 1991, pp.45-47.
- Quitmeyer, Joann, "New Technology Alkaline Cleaners Replace Chlorinated Solvent Degreasers," Lubrication Engineering, March 1991.
- Scislowski, Stan, "Cleaning Basics: Part I -- Introduction," Metal Finishing, Vol. 88, No. 1, Jan. 1990, p.33.
- Scislowski, Stan, "Cleaning Basics: Part II -- Soils," Metal Finishing, Vol. 88, No. 2, Feb. 1990, pp.43-46.
- Scislowski, Stan, "Cleaning Basics: Synthetic Detergent and Cleaner Selection," Metal Finishing, Vol. 88, No. 3, March 1990, pp.51-52.
- Scislowski, Stan, "Cleaning Basics: Alkaline Cleaners," Metal Finishing, Vol. 88, No. 4, April 1990, pp.23-25.
- Scislowski, Stan, "Cleaning Basics: Emulsion and Solvent Cleaners," Metal Finishing Handbook, Vol. 88, No. 5, May 1990, p.63.
- Spring, Samuel, Metal Cleaning, New York: Reinhold Publishing Corp., 1963.
- Temple, Stephen D., "A New Era for Aqueous Cleaning," Products Finishing, March 1990, pp.76-83.

REFERENCES (continued)

- "Terpene Solvents Prevent Ozone Risk," American Machinist, Jan.1989,pp.25-27.
- Tool and Manufacturing Engineers Handbook, Vol 3 -- Materials, Finishing and Coating, Ed. by Charles Weck and Raymond F. Veilleux. Dearborn, MI: Society of Manufacturing Engineers, 1985.
- United States Environmental Protection Agency, ICOLP Technical Committee. Alternatives For CFC-113 and Methyl Chloroform in Metal Cleaning, USEPA, June 1991, EPA/400-1-91-019.
- United States Environmental Protection Agency, ICLOP Technical Committee. Eliminating CFC-113 And Methyl Chloroform in Precision Cleaning Operations, USEPA, June 1991, EPA/400/1-91/018.
- United States Environmental Protection Agency, Guide to Clean Technology: Alternatives to Chlorinated Solvents For Cleaning And Degreasing, USEPA, July 1992.
- United Stated Environmental Protection Agency, Guide to Clean Technology: Cleaning and Degreasing Process Changes, USEPA, May 12, 1992.
- United States Environmental Protection Agency, Office of Toxic Substances. Aqueous and Terpene Cleaning Interim Report, Washington, D.C.: USEPA, November 15, 1990.

For more information on waste reduction for businesses and the Small Business Clean Air Assistance Program, contact the:

Environmental Services Division
Michigan Departments of Commerce and Natural Resources
P.O. Box 30004
Lansing, Michigan 48909
(517) 335-1178

Toll Free:
1-800-NO-2-WASTE

October 1994
#9409