Closing the Loop on Cleaners

Cleaning is a universal step in the finishing world, so its impact on the environment is a major concern . . .

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arious cost factors and governmental regulations are forcing industry to re-examine how it conducts business. This is especially true for the finishing industry, where air and water emissions are concerned and toxic and hazardous materials are used.

The foundation of any finish, and the first step in all pretreatment operations, is cleaning. Since cleaning is a universal step, its impact on environmental and cost issues is a major concern.

Cleaners. Production cleaning operations typically include vapor degreasing, pressure spraying and liquid immersion. Mechanical means such as agitation, ultrasonics, brushing and hand wiping may be employed, along with heat, to accelerate or complete cleaning.

Cleaners fit into three classes: solvents, semi-aqueous and aqueous. Solvent-based cleaners, both vapor and immersion, are being phased out wherever possible due to safety concerns and environmental regulations. Semi-aqueous cleaners are an emulsion of water, organic solvents and emulsifiers. They have limited applications and usually are followed by alkaline cleaning to remove solvent traces. Semi-aqueous cleaners do not normally lend themselves to on-site recycling and are either disposed of or returned to the supplier.

Aqueous cleaners are by far the largest group, and their use is growing. Aqueous cleaners fit into three major groups: acid cleaners, detergent cleaners and alkaline cleaners. Acid cleaners are based on diluted concentrations of either organic or inorganic acids such as gluconic, citric and phosphoric. These are used when light-metal oxides are present or other special conditions warrant, such as a polymerized oil film.

Water-soluble solvents, along with wetting and emulsifying agents, are commonly added to remove oils and other soils. Formulations are now available using mixtures of hydrophilic and lipophilic surfactants in place of solvents. The type of acid and additive packages used depends on the base metal, type of soil and post treatments. The makeup of an acid cleaner and the contaminant involved determine the viability of recycling and final disposal. High acid concentrations used for pickling and/ or activation may also be classified as acid cleaners.

Detergent cleaners are neutral cleaners, since they are neither acid or alkaline based. They are also solvent-free and environmentally friendly, especially when phosphates and nitrates are not included. They normally include sequestering agents, dispersants, buffering salts, wetting agents and sometimes soaps. High concentrations and elevated temperatures make their use somewhat limited, but they are normally effective for removing residue on buffed metals. They can have an impact on overall toxicity limits, as well as foaming, when they are discharged.

Alkaline aqueous cleaners are the most widely used. The simplest forms use sodium or potassium hydroxide, possibly with carbonates and/or silicates. In the past, kerosene or mineral spirits have been added for many applications. Today, these solvents are often replaced with higher additions of surfactants, wetting agents, sequestering agents and dispersants. In some instances, defoamers and rust inhibitors are also included.

These non-hazardous additives can eliminate the environmental concerns caused by solvents. However, surfactants and other organic additives, though not oils, may cause problems for direct dischargers and those whose sewer systems are imposing tighter limits on organics and overall toxicity.

Recycling. There are many reasons to close the loop on cleaners, including environmental, production and economics. These can be broken down as follows:

Environmental: Conserves chemicals; Reduces or eliminates discharge of toxic or hazardous materials; Step toward zero discharge; Less contamination in rinse waters; and Recycles oils.

Production: Consistent cleaning; Higher throughput; and Fewer rejects.

Economics: Savings in both cleaner and waste treatment chemicals; Reduced labor costs; Lower sludge disposal costs; Possible sale of recovered oil.

Preliminary Steps. The first step in closing the loop is to extend the working life of the cleaner by removing contaminants and retaining active ingredients. The second is to concentrate both contaminants and cleaning agents so water can be recycled.

To extend cleaner life, first identify and quantify the contaminants. These are the solids or by-products formed by the reaction of cleaning chemicals with parts or soil. Organic and inorganic contaminants require different treatments. Organic materials include oils and grease. Waxes may also be present, along with other residues. Inorganic materials typically consist of dirt, oxides, salts and scale.

Next, the types and amounts of con-

taminants brought into the cleaner bath must be minimized. For example, minimize the use and amount of lubricants employed in stamping, forming and machining prior to cleaning. Precleaning the parts prior to welding will minimize the formation of hardto-remove carbonaceous materials.

Parts should also be protected during in transit and storage. Dirt increases the load on the bath and oxides increase cleaning steps or cause changes in the cleaner formulation. Excessive salts will hinder bath effectiveness, increase rinsing requirements and cause poor film adhesion or interfacial corrosion.

The third step is to identify cleaner composition and decide what options are available if precleaning operational changes are made. This will require the assistance of a chemical supplier.

Bath Extension. It is now possible to investigate ways to extend cleaner life. The contaminant removal chart (Table I) shows typical contaminant types and ways to remove them. How effective these approaches are depends on many factors, but the most critical is the cleaner formulation.

Basic Separation. The basic aqueous cleaner bath is dumped every one to four weeks due to solids buildup in the bottom of the tank, tramp oil on the surface and emulsified oils in the solution.

Bath life may be extended two to three times by removing solid and free oils and grease through a combination of the approaches in Table I. Chemical additions must still be made in order to replace those dragged out on parts. Figure 1 shows a typical flow diagram of this approach.

Extension of the bath for longer periods requires control of emulsified and dissolved materials. In Table I, there are two approaches that can remove emulsified oils under the proper conditions. The first is batch application of heat, along with a cleaner formulation designed to release oils so they may be skimmed off after the emulsion bond is broken. Separate tanks, transfer pumps and a reserve capacity of uncontaminated cleaner are required so the line is not out of service for the 12 to 36 hrs that this operation may involve.

Membrane Separation. A better approach uses crossflow membrane separation in either micro- or ultrafiltration porosity ranges for emulsion splitting. This may extend cleaner life by a factor of ten or more. Early efforts with this technology often met with poor results because of the limited variety of membranes, reluctance of cleaner suppliers and lack of understanding of the mechanisms affecting membrane performance and fouling.

Experience, cleaners formulated with recycling in mind and recent developments in membrane technology, have helped close the cleaner loop. This work has involved both organic- and inorganic-based membranes. The variety of membrane materials that can be used for cleaner recycling and disposal is shown in Table II.

Polymeric Membranes. With new chemicals and solvent- and temperature-resistant polymeric materials

available, membrane filtration can be used on many cleaners and waste applications, even up to 70C. These new materials have been enhanced by various patented processes that amplify their hydrophilic nature, increasing flow capacity and passage of desirable cleaner components while rejecting free and emulsified oils.

The most common and cost-effective polymeric membrane configuration is a spiral-wound module. Care must be taken to minimize plugging. This is accomplished with prefiltration in the 50 to 150 micron range and limiting process concentration. Polymeric materials must be carefully matched to the process solution, contaminants and cleaning chemicals. Some membranes are available in a tubular configuration, permitting greater solids loading and higher viscosities. In either configuration, oil concentrations should not exceed 30 to 40 pct.

Polymeric membranes are usually supplied in thermoplastic (PVC, CPVC, PP), thermosetting plastic (FRP) or stainless steel housing to match operating conditions and cost objectives.

Inorganic membranes consist of ceramic materials on either carbon or ceramic supports, or an all-composite carbon. These materials exhibit resistance to all solvents, oil and most chemicals through the full pH range and operating temperatures of 250F or more. Chemicals, solvents and temperature limits are more related to seal and housing materials than membrane materials, except for hydrofluoric acid with ceramics and hot

concentrated caustic with alumina. An inorganic membrane housing is usually made of 304 or 316 stainless steel to match the high temperature and solvent-resistant capabilities of the membranes themselves. But this limits their use in high-chloride streams.

System Selection. Each membrane system must be examined for cleaner composition, soil loading, fouling characteristics, operating parameters, capital costs, operational costs and systems payback.

Initial recommendations may be based on empirical knowledge. However, it is best to narrow choices down to the best one or two membranes. Small samples of one liter or less of contaminated cleaner can be processed through each membrane. The permeate is then analyzed for soils and active ingredients.

If possible, these potential membranes would then be piloted on the process to confirm long-term performance under operating conditions. This pilot work would normally entail a short trial of each membrane, followed by running the most promising selection four to 12 weeks to verify long-term flux rates and cleaning process.

The recycling system can be fitted to existing or new single-stage or multi-stage systems, as shown in Figure 2. The cascading multi-stage cleaner line is preferred, since a highsolids concentration can be maintained in stage one and less "clean" permeate is required in stage two to maintain low soil levels. The combination of higher feed concentrations

and lower permeate flow allows for a smaller, less costly system.

Approaching a true closed loop (Fig. 3) on the cleaner line requires the use of three or more cascading rinses after the last cleaner, with the first rinse cascading into the cleaner itself. This returns solids and active ingredients that were dragged out back to the cleaner. Extra attention must be paid to the quality of the water used for rinses and makeup. Any dissolved materials will build up in the cleaner and require premature disposal.

Final Disposal. The second phase of closing the cleaner loop is disposing of the spent cleaner bath. Current practice is to direct this material to waste treatment where it is mixed with other oily wastes. Free oil is then removed and chemicals are added to break the emulsions so oil can be floated out or bound up with the chemicals and removed as a sludge. If combined volumes are small enough, they may be batch treated with chemicals and/or heat, the oil skimmed off and the water discharged for further treatment. Typically, a floating rag layer forms a stable water-in-oil emulsion and floatable solids that must be scraped off periodically and drummed for disposal.

These approaches require varying amounts of chemicals and are labor and equipment intensive. The oil removed is costly to dispose of or requires further treatment to recover. The water phase usually meets discharge limits for sanitary sewer systems, but demands further treatment for direct discharge.

A better way to dispose of the

spent cleaner uses a membrane system similar to that used in the cleanerrecycling operations. In a simple unit. the spent cleaner goes into the circulation tank and is pumped through the membrane modules. The type and porosity of the membranes are matched to the makeup of the exhausted cleaner and discharge limits.

Spent cleaners and other oily wastes are collected and filtered to remove large solids and abrasive materials before they enter the circulation tank. The tank is constantly replenished as permeate is discharged. Free oil is removed from the circulation tank as it forms. When the oil concentration approaches the working limit of the membranes, the feed to the circulation tank stops and additional permeate is bled from the loop until maximum concentrations are reached. This concentrated material, which will be 30 to 60 pct oil, can be pumped to an evaporator for further denaturing or to a waste oil holding tank.

Periodically, a cleaning operation from a separate solution tank is performed to clean the membranes. This is normally done at the end of each concentration cycle.

The filtrate will normally require pH adjustment prior to discharge, due to the alkaline nature of most cleaners. For recycling as rinse water, further treatment by absorbents, adsorbents, nanofiltration or reverse osmosis or a combination, would be required to close the loop. For direct discharge to receiving streams with low organic and toxicity limits, biological or advanced oxidation treatment should also be employed.

Membranes will play an ever greater role in the goal of closing the loop on cleaners. Selecting the correct system and chemical suppliers is as important, if not more so, than the initial choice of membranes. Working together, the quality of the final product is maintained while resources are conserved, waste is minimized and environmental laws are complied with at reduced operating costs. **PF**

Captions:

1. BASIC AQUEOUS DEGREASING with solids or organics removal

- 2. MULTI-STAGE aqueous degreasing recycling loop
- 3. MULTI-STAGE aqueous degreasing closed-loop recycling system

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TABLE I—Contaminant Removal Methods

Type Solids	Approach Clarification, Filtration Hydrocyclone, Centrifuge	
Free Oil And Grease (Fog)	Skimming, Gravity Separator, Coalesence, Hydrocyclone, Centrifuge	
Emulsified Oils	Micro or Ultra Filtration, Heat (Than As Fog), • Chemical (Than As Fog) • Adsorption, • Absorption	
Solvents Immiscible	See Fog	
Solvents Dissolved	Ultra or • Nano Filtration, • Reverse Osmosis, • Evaporation, • Adsorption, • Absorption, • Biological, • Advance Oxidation	
Organics	See Solvents	
Salts	Ion-Exchange, • Reverse Osmosis, • Evaporation • Nano Filtration	
BOD's, COD's	Reverse Osmosis, Biological, Advance Oxidation	
Not Used For Recycling of Cleaner Baths		

TABLE II—Membrane Materials and Applications

Application E-Coat Paint	Type Polymeric	Configuration Spiral Wound, Tubular
Cleaner Recycling	Polymeric Inorganic	Tubular, Spiral Wound, Hollow Fiber Tubular
Oily Wastes	Polymeric Inorganic	Tubular, Spiral Wound, Hollow Fiber Tubular
Heavy Metal Wastes	Polymeric	Tubular
Rinse Recycling	Polymeric Inorganic	Tubular, Spiral Wound, Hollow Fiber Tubular (Pretreat Only)