Microfiltration of Aqueous Cleaner Solutions

By Dave Peterson

This edited version of a paper presented at the 16th AESF/EPA Pollution Prevention and Control Conference, held February 13–15, 1995 during AESF COMPLIANCE WEEK, will focus on the fundamentals of aqueous cleaner chemistry and microfiltration. Basic surfactant chemistry will be discussed to provide an understanding of how grease and oils exist in aqueous solutions. Various types of filtration will be covered, with particular attention given to crossflow. Actual case study information will be presented concerning the use of microfiltration at Modine Manufacturing Company in Racine, WI.

Aqueous cleaning has been the primary substitute for chlorinated solvents. Although more benign than chlorinated solvents, aqueous cleaning has problems of its own. A cleaner, for example, may be initially non-hazardous and biodegradable, but after its useful life, may be loaded with oil and grease from metalworking fluids and lubricants.

Oil Contamination

Oil exists in three forms in an aqueous cleaner: Tramp oil, mechanically emulsified oil and chemically emulsified oil. Tramp oil represents the majority of oil from the parts and is the easiest to remove—usually by using a simple skimmer.

Mechanically emulsified oils are similar to tramp oils, but have been broken apart by agitation forces encountered with pumping, basket movement, and drainage. If the bath is allowed to sit quietly, much of this oil will eventually float out of solution. Coalescing equipment exists that will speed this process through agglomeration of the oil droplets that will then want to separate as a result of differences in density.

Chemically emulsified oil is that which is permanently suspended by the cleaner. The surfactants in the cleaner are supposed to emulsify and suspend this oil to avoid redeposition. The most viable option currently available for the removal of this oil is microfiltration.

Aqueous Cleaning Chemistry

Aqueous cleaners will typically consist of three different categories of ingredients: Builders, surfactants and additives. Each serves a unique function in the process tank.

Builders are inorganic alkaline salts and serve a number of functions, such as buffering action, saponification of fatty soils, softening water and synergistically boosting surfactant performance. Builders are usually carbonates, phosphates (often complex), silicates, and, if compatible with the metal, hydroxides. With the exception of silicates, all dissolve into solution. Silicates may not go completely into solution initially, and when neutralized they form silicic acid, which exists as a colloidal precipitate.

The types of additives include sequestrants, chelants and dispersants. They perform a variety of functions, such as softening water, dispersing finely divided soilds and particulate, and suspending dissolved solids.

Surfactants play a significant role in any aqueous cleaner. They are unique chemicals in that they have two "ends." One end of the surfactant is polar or water soluble (known as hydrophilic), while the other end of the molecule is nonpolar or oil-soluble (known as lipophilic). This unique property is what makes surfactants so valuable for solubilizing oil in aqueous cleaners. Poor selection of these can adversely affect the cleaner more significantly than any of the other categories.

There are four types of surfactants: Cationics are usually found in germicides and fabric softeners; amphoterics will usually serve only specialty purposes in cleaners, such as hydrotroping less soluble cleaner compounds; and anionic and nonionic surfactants are those most frequently found in industrial cleaners.

Anionic Surfactants

These surfactants include sulfates, sulfonates and phosphate esters. Typical properties are:

- Hydrotroping less soluble species;
- Not being temperature-dependent;
- Higher foaming;
- Solubilizing polar soils.

Nonionic Surfactants

These include nonylphenolethoxylates and primary alcohol ethoxylates. Typical properties are:

- Lower foaming;
- pH-resistant;
- Temperature-dependent;
- Solubilizing nonpolar soils.

How Oil is Emulsified In an Aqueous Solution

Surfactants "surround" the oil and suspend it to create an emulsion. This is possible because the lipophilic end of the surfactant is solubilized by the oil, while the hydrophilic end is solubilized by the water. Because of this, the emulsion created is very stable and will not separate through conventional means (quiescent tank or coalescing equipment). The microfilter membrane must remove this emulsified oil through exclusion.

Filtration Nomenclature

Filtration Regions

Filtration regions may be broken up into the size particulate they are meant to remove. Particle filtration will typically refer to filtration of macroscopic particles. This will usually be from about 10 to greater than 1500 microns.

Microfiltration refers to the filtration of microscopic particles, usually in the range of 0.1 to 5 microns.

Sub-micron filtration (anything less than 0.1 microns) will involve ultrafiltration, nanofiltration and reverse osmosis. Note: These ranges are approximate; various sources will quote slightly differing ranges.

Absolute & Nominal Ratings

There are two ways a filter or membrane can be rated for its removal efficiences. A nominal porosity rating means that most, but not all particles, greater than the stated porosity rating will be retained by the filter. Usually 98 to 99 percent or more will be retained. In some cases, that type of removal is not satisfactory. This is when a filter with an absolute porosity rating is necessary. An absolute porosity rating will insure than all particles greater than that rating will be removed.

Crossflow vs. Traditional Filtration

Traditional (normal) "dead end" filtration is where the entire feed stream is forced to pass through the filter. Crossflow filtration flows the feed stream across the membrane with the permeate flow being tangential to the flow of the feed stream (Fig. 1).

Crossflow filtration is generally reserved for microfiltration, ultrafiltration and reverse osmosis. Because all the feed stream does not pass through this filter, the system has to operate under elevated pressures to force the filtration to occur. Crossflow microfiltration will typically operate in the 20 to 50 psi range; ultrafiltration in the 50 to 200 psi range; and reverse osmosis from 200 psi to as high as 1000 psi.

Depth vs. Surface Filters

There are two ways a filter can be constructed. A depth filter has a thick, fibrous matrix to trap the particles. A surface filter is a thin membrane that acts as a barrier to retain particles over a specified size (Figs. 2 and 3). Depth filtration will always utilize a dead-end type of filter. Surface filtration can utilize either a crossflow or a dead-end filter.

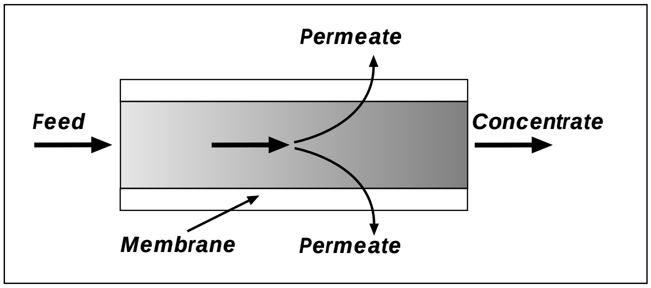

Fig. 1—Illustration of crossflow filtration in a tubular membrane.

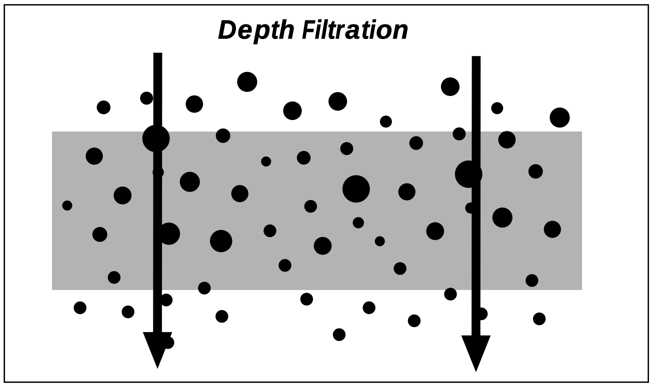

Fig. 2—Depth filtration.[1]

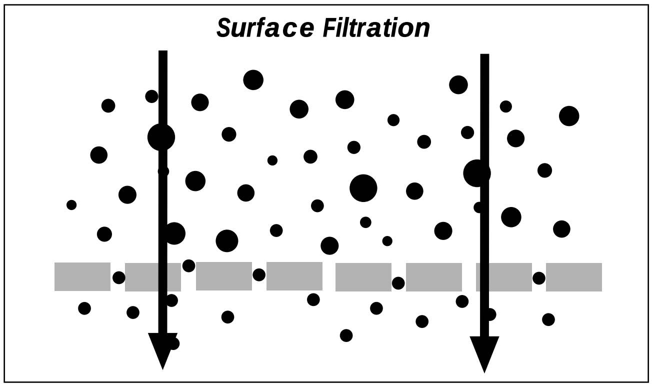

Fig. 3—Surface filtration.[1]

Particulate Filtration

Particulate filtration is used for the removal of macroscopic-sized particles from liquids. This usually is in the size range of 10 to 1500 microns. Methods include sand filtration, basket strainers and screens, bag filters and depth filters.

Sand Filters

Sand filters are relatively inexpensive means of processing large amounts of fluid. Damage to the media is unlikely. Stratification of sand can occur that may create premature plugging or could allow smaller particles to pass through it. Range of removal is usually from about 1500 down to about 100 microns. Sand filters are often used as a prefilter for further membrane filtration.

Strainers

Basket strainers and screens exist for large particle removal. They are useful for the removal of metallic chips and other large particles upstream from pumps and other equipment that could be damaged from such debris. Construction is usually stainless steel and plastics (PVC, CPVC and polypropylene). These are typically rated as some fraction of an inch or a given mesh size. The larger the mesh size rating, the smaller the filtration range will be. Although strainers are more often used for coarse filtration, they can get as low as 100 microns.

Bag Filters

Bag filters are constructed of a woven cloth or plastic media (often polypropylene, polyethylene or nylon). Some can be removed and cleaned, while others are disposable. Filter size ranges from about 800 down to about 10 microns. A few bag filters can go lower than this, although it is arguable whether a different type of filter should be used in this range.

Depth Filters

Depth filters are typically contructed of continuous wound materials (cotton, polypropylene, polyethylene, acrylic, etc.), porous polypropylene fibers and pleated polypropylene membranes. These materials are manufactured to give a filter with thick walls and a complex path for the liquid to flow through. The particles are then trapped in this thick media.

Depth filters have a fairly wide range of use and can be found with nominal porosity ratings from more than 75 microns down to about one micron for a few high-quality pleated membrane filters. Depth filters have a tendency to plug before the majority of surface area has been utilized.

A more effective, longer life depth filter is one that is known as a graded density. This is manufactured with a gradual increase in density toward the inside of the filter. Because it has a tendency to screen out larger particles first, it has a higher particle-loading capacity. Because the particles have to be trapped in the dense media, occasionally particles larger than the nominal porosity rating can get through. The filters are usually disposed of after use.

Microfiltration

Microfiltration is used for removal of particles in the microscopic range. Although various sources will specify different ranges, it can typically be considered to be from about 0.1 to 5 microns. Depth filters can be found only in the higher end of this range. Surface filters are necessary to achieve the lower micron ratings.

With surface filtration, a thin membrane acts as a porous wall or barrier for micro-particulate filtration. Because of the design, absolute micron ratings are possible. Surface filters can take the form of a pleated flat polymeric membrane, a flat, spiral-wound polymeric membrane or a tubular ceramic or polymeric membrane. These are designed to increase their surface area for more effective filtration. The primary advantages of these is the low micron ranges that can be achieved, as well as a higher degree of precision through the ability of the filter to obtain an absolute micron rating. Microfiltration is the type of filtration most often used in recycling aqueous cleaner baths.

Submicron Filtration

This range of filtration is characterized by the removal of submicron particles, from ions to 0.1 microns in size. These are only visible with the aid of a scanning electron microscope (SEM). This encompasses the range of ultrafiltration, nanofiltration and reverse osmosis.

Ultrafiltration

Ultrafiltration is in the range of 0.005 to 0.1 microns. It is similar to microfiltration in many ways, and for that reason, the border between the two is often blurred. Ultrafiltration can use pleated membrane surface filters on the high end of the porosity range. Spiral-wound surface filters and tubular filters can be used to cover most of the ultrafiltration range and are more common. The tubular filters can be of a polymeric or ceramic design. Ultrafiltration will sometimes be used on the higher end of its porosity range for the recycling of aqueous cleaning baths. Another application of this membrane filtration is for the recycling of rinsewater from process lines. Although this will extend the effective life of the rinsewater, it cannot remove ions that can be found in both acid and alkaline cleaners, as well as plating solutions. These can only be removed through reverse osmosis.

Nanofiltration

Nanofiltration covers a relatively small porosity range that bridges the gap between ultrafiltration and reverse osmosis. This can typically be thought of as 0.001 to 0.005 microns. Because of this small range, many filter system manufacturers tend to neglect this as even being a separate category and will often talk in terms of going directly from ultrafiltration to reverse osmosis.

Reverse Osmosis

Reverse osmosis is reserved for only the most stringent filtration requirements because it operates in the ionic range (usually less than 0.001 microns). One application is for the recycling of rinsewater (usually in conjunction with ultrafiltration). Spiral-wound membranes or tubular designs are frequently utilized. Membranes are of a polymeric nature.

Use of Microfiltration At Modine Manufacturing

With an increasing number of aqueous cleaning baths coming on-line throughout many of Modine's plants, a means of recycling them to extend the frequency between tank dumps needed to be investigated. This was begun in February 1993 by first doing an industry-wide search of manufacturers of turnkey aqueous cleaner micro/ultrafiltration units. At that time there was not near the number there is today. Literature was reviewed and visits made to see some units. It was discovered that there were two basic types of membranes (polymeric and ceramic) and two basic modes of filtration (traditional "dead-end" and crossflow).

The uppermost operating parameters for the polymeric membranes is typically 71 °C to 77 °C (160 °F to 170 °F) and a pH of about 11 or 12. Many metalworking plants require heavy duty alkaline cleaners to remove the soils generated from their operations. These aqueous cleaners are usually operated at 77 °C to 82 °C (170 °F to 180 °F) and at an elevated pH (often above 12). The use of these cleaning solutions required the use of the more robust ceramic membranes that can be operated greater than 100 °C (212 °F) and at both pH extremes.

The ceramic filters had some other advantages, such as utilizing crossflow filtration, which allows the membrane to stay clean longer because the feed stream flows across the membrane. Another advantage of the ceramic filter is rigidity. With crossflow filtration, the build-up of what is known as a dynamic layer can occur (contaminants on the wall of the membrane). The rigidity of ther ceramic membrane allows them to be reverse-flushed ("backpulsed") under pressure while in operation. The purpose of this is to get rid of some of the dynamic layer, again extending the life of the filter that much longer. Many polymeric membranes do not have the rigidity to stand up to this.

Small-scale Pilot Testing at Modine

Once it was determined that a ceramic membrane would be required, it was decided that a small-scale laboratory pilot test system would be built to further test this technology. With some technical input from a filter manufacturer and assistance from the Modine Engineering Services Department, we were able to design and build such a benchtop system. There were several reasons for building this system in-house. The following goals were defined and accomplished:

- Gain a better understanding of microfiltration;
- Develop and prove out a unique method of backpulsing the membrane;
- Evaluate the effectiveness of microfiltration at different porosities with Modine's current aqueous cleaners;
- Determine whether aqueous cleaner components were being removed (throughout the range of these porosities) and if so, attempt to identify and quantify;
- Retain the pilot system at the corporate labs for use in feasibility studies for each specific Modine manufacturing facility interested in this technology.

Full-Scale Pilot System

With the success and knowledge gained from building the bench-scale microfiltration unit, the scale-up to a full-sized system was much easier. The goals for this, the second phase of the project, were as follows:

- Specify all parameters that would require scaling up (pumps, piping, controls, etc.);
- Build a full-scale system in-house that was either less expensive than available turnkey systems or equally priced, but contained more value-added features;
- Make this system available to all Modine plants interested.

The scale-up from the bench-top pilot system was successful. Pipe velocities, pressures, backpulsing and other controls worked very well and as specified. The Materials and Process Engineering Department was successful with its second goal in that a better system was developed and built at a lower price than other ceramic turnkey systems available at the time.

The third goal was accomplished in that the filter system has been to three plants with more interest in trials of their own, once the unit becomes available. This alone should pay for the cost of this pilot system. Typically, turnkey filter system companies will enter into a lease agreement with interested parties, although the cost of these trials can be very high. Costs can range from $1,000 to $2,000 a month. Because the system was on test for more than seven months at these various facilities, this has essentially paid for the development cost of the unit.

The Future for Modine Manufacturing

The Modine Materials and Process Engineering Department will disseminate information throughout the manufacturing facilities to inform them of the existence of this piece of pilot equipment that is available for their evaluation. As plants try this equipment, they will determine whether or not they want to pursue microfiltration of their own aqueous cleaner baths. If the decision is made to pursue this technology, they would have the option of purchasing a system from a turnkey manufacturer or from Modine corporate.

The Materials and Process Engineering Department will also continue to do feasibility analyses on various waste cleaner samples from the plants. They will continue to evaluate different cleaner systems in combination with various lubricants. Another goal will be to further take cost out of the manufacturing of these microfilter units internally, making it that much more advantageous for Modine to build these systems internally.

Reference

1. "Pleated Cartridge Filters," Form P/N 40892 Rev A, p. 2, Minnetonka, MN 55343.

Next month: An edited version of the follow-up paper Peterson presented at COMPLIANCE WEEK '95 will be included. The subject is "Limitations of Microfiltration."

About the Author

Dave Peterson is supervisor of Corrosion and Chemical Engineering in the Materials and Process Engineering Department at Modine Manufacturing Company, 1500 DeKoven Avenue, Racine, WI 53403. His responsibilities include specification and formulation of process chemicals, specification and building of process chemical equipment and corrosion testing equipment, in addition to troubleshooting, process development and waste minimization for Modine's North American facilities. He has been involved with all vapor degreaser replacement projects throughout Modine. Peterson has written several papers in the areas of process chemistry, waste minimization and microfiltration.