To make use of microfiltration’s fullest potential, its drawbacks and limitations must be understood. A major problem is the tendency for microfiltration to remove aqueous cleaner constituents. Filter system manufacturers do not have the necessary chemical expertise to identify this problem. Chemical cleaner manufacturers lack the necessary knowledge of filter systems and show little interest, because it may represent a loss of revenue for them. This edited version of a presentation at the 16th AESF/EPA Pollution Prevention & Control Conference, held February 13–15, 1995, at Orlando, FL, presents theory and research showing that cleaner depletion is inevitable. Peterson advocates a cooperative effort between filter system and cleaner manufacturers to fully exploit microfiltration technology. For more on this subject, see “An Introduction to Microfiltration of Aqueous Cleaner Solutions,” by Dave Peterson, in the April issue of P&SF.

The phase-out of ozone depleting solvents has created a void in the area of industrial cleaning. This void has, in large part, been filled by aqueous cleaning systems. The use of this alternative has been an effective substitute, although it has created environmental problems of its own. These cleaning solutions become loaded with oils from sources such as metal-working lubricants and rust inhibitors. The resultant oil-rich aqueous solution may be considered hazardous and can be very expensive to treat, if disposed of. For this reason, recycling of these aqueous cleaning tanks is important for both environmental and economic reasons.

Currently, the leading candidate to accomplish this is microfiltration (often complemented by a skimmer and/or a coalescer). If used on-line, this also has the benefit of maintaining the cleaner at a consistent level of quality. Rather than charging a bath and observing the steady decline in its performance, microfiltration can remove oils and keep the bath in a steady state.

Microfiltration may have limitations of its own, though. By the nature of its operation, it is possible to remove certain cleaner components. To understand how this is possible, it is first necessary to understand basic surfactant chemistry.

**Surfactant Chemistry**

Surfactants 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 non-polar or oil soluble (known as lipophilic).

Because of their structure, surfactant molecules do not exist alone in solution except at very low concentrations, where, even then, they are usually in pairs or small groups. They are ineffective in this form and do not display good surface active properties. As more surfactant is added, the groups grow into a larger organized structure known as a micelle. The organization of this structure is such that the hydrophilic ends of the groups are facing outward, and the lipophilic ends are turned in toward the center of the micelle (in the case of a water solution). In an oil base medium they are oriented just the opposite. This orientation is natural because it minimizes the free energy of the system. (See Figure 1.)

![Fig. 1—Surfactant micelle formations.](image1)

![Fig. 2—Solubilization of oil on/in a surfactant micelle.](image2)

When there are enough surfactants in solution (almost all of them exist in micellar form), they have reached what is known as the critical micelle concentration, or CMC. This is the minimum concentration necessary for a surfactant to display its properties. The CMC is often determined experimentally through surface tension measurements.

**Solubilization of Oil In an Aqueous Solution**

Solubilization of oil takes place on or within the micelle structure. There are four different areas where solubilization can occur. They are:

1. At the micelle/water interface.
2. Between hydrophilic groups.
3. In the palisade layer, between the hydrophilic and hydrophobic group.
4. At the inner core of the micelle.

Highly polar molecules will typically reside at the micelle/water interface. Molecules with mixed polarities (e.g., a long chain alcohol) will usually reside within the palisade layer with the polar alcohol group oriented outward toward the hydrophilic end of the micelle. The ratio of polar to non-polar entities within the molecular structure will determine the depth of penetration into the palisade layer. Longer chain (and typically less polar) molecules will reside deeper within the palisade layer. Completely non-polar molecules...
(e.g., a paraffinic mineral oil) will reside entirely within the inner core of the micelle. Figure 2 illustrates these locations.

**Oil Removal**

It is necessary to understand micelle structure, formation and oil solubilization to understand how microfiltration works in removing emulsified oil from solution. The size of the surfactant micelle will grow to some extent as oil and contaminants are solubilized by them. The micelle structure typically is very stable, because of the natural “desire” of the system to be at its lowest point of free energy. Because of this, the emulsion created is very stable and will not separate through conventional means (quiescent tank or coalescing equipment). It is, therefore, the job of the microfilter membrane to remove this emulsified oil through exclusion. The filter will not allow micelles that are larger than the nominal porosity of the filter to pass through to the permeate stream. Those micelles that have solubilized oil within them are larger, and therefore have a greater tendency to be retained on the concentrate side of the filter. Figure 3 better illustrates this.

**Surfactant Removal**

A general relationship can be inferred between the porosity of filters and the molecular weights they will remove. For instance, if ultrafiltration is in the range of 0.005 to 0.1 microns, this would be roughly equivalent to an approximate molecular weight range of 10,000 to 200,000. The range for microfiltration (0.1–5 microns) would roughly approximate molecular weights of 200,000 to more than 1 million.

Considering these porosities and molecular weights, there could be cause for concern that some additives may be removed from solution. Certain additives are included that serve the function of dispersing and suspending contaminants to keep them from redepositing on the workpiece. Many times these additives will be in the form of a sodium salt of a maleic/acrylic acid copolymer. The molecular weights of these copolymers can range from about 15,000–150,000. Considering this, it is reasonable to believe that some would be removed below membrane porosities of 0.1 micron.

Surfactants are another cause for concern. If they existed singularly in solution, there would never be reason to believe any would be removed, based solely on their molecular weights. Molecular weight ranges for various subclasses of typical anionic and nonionic surfactants can be found in Table 1.

### Table 1: Approximate Molecular Weight Ranges For Various Classes of Surfactants

<table>
<thead>
<tr>
<th>Surfactant Type</th>
<th>Approximate MW</th>
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<tbody>
<tr>
<td>Phosphate Esters</td>
<td>500</td>
</tr>
<tr>
<td>Sulfonates</td>
<td>300–500</td>
</tr>
<tr>
<td>Sulfates</td>
<td>300–500</td>
</tr>
<tr>
<td>Nonylphenols Ethoxylates</td>
<td>600–1,500</td>
</tr>
<tr>
<td>Alkoxylated fatty alcohols</td>
<td>600–1,000</td>
</tr>
<tr>
<td>Block Copolymers</td>
<td>4,000–8,000</td>
</tr>
</tbody>
</table>

Given this, the smallest porosity ultrafilter would not remove even the largest of the surfactants if they existed alone in solution. Surfactants, however, exist in groups known as micelles. The number of individual surfactants within a micelle is called its aggregation number. In general, the greater the dissimilarity between the surfactant and the solvent, the larger the aggregation number. This is understandable from the point of minimizing the free energy of the system. As an example, an increase of the lipophilic chain on a surfactant in an aqueous solution will increase the aggregation number of the micellar system. An increase in the hydrophilic chain will cause a decrease in the aggregation number in an aqueous solution. In general, anionics tend to have smaller aggregation numbers than nonionics.

**Aggregation Numbers**

Some reference to aggregation numbers can be found in the literature. The aggregation numbers stated are often for a single surfactant at room temperature with no other organics or electrolyte present. Under these conditions, aggregation numbers for anionics will typically be in the range of 25 to 50 in water. Nonionic aggregation numbers can vary much more widely, depending on their structure. Those that would be found in an aqueous cleaner may be in the range of 100 to 500.

The above numbers show how the molecular weight of a micelle will grow in solution. This does not reflect the true nature of the situation, though, because the conditions above are not typically found in an aqueous cleaner. Those conditions will generally involve high temperatures, a high electrolyte loading caused by inorganic builders, mixtures of surfactants and surfactant types, and the presence of hydrocarbons (from the contaminants being removed). These factors will significantly affect the aggregation numbers of the surfactants, usually increasing them.

While temperature does not have an important role in anionic micelle aggregation, it is very significant to
nonionic aggregation numbers. As the temperature of the solution is increased, the aggregation number continues to grow. The ethylene oxide chain on the nonionic starts to straighten out, which eliminates the effect of hydrogen bonding with water. This is what keeps the surfactant in solution. (See Fig. 4.)

As the temperature increases, more surfactants “join” the nonionic micelle to keep it in solution. At a temperature called the cloud point, the surfactant micelles are so large that they start to come out of solution and make the liquid turbid (therefore, the name “cloud point”). Figure 5 illustrates the increase in aggregation number vs. temperature for a particular nonionic surfactant.

The presence of an electrolyte most significantly influences anionic surfactants by causing an increase in aggregation number. This may double or triple the aggregation number. The literature is unclear on how an electrolyte affects the nonionic surfactants. In some cases, the aggregation number is increased; other times it is decreased.

The presence of hydrocarbons from metalworking fluids is almost a constant condition. As the micelle (anionic or nonionic) solubilizes these contaminants, the aggregation number will rise, resulting in a larger micelle.

Many aqueous cleaners will contain both anionic and nonionic surfactants, often more than one of each. They will go into solution to form what are known as mixed micelles. These will contain two or more surfactants. The resulting aggregation numbers will also be influenced in some way by all the above conditions, likely creating a mixed micelle larger than the individual surfactant micelle.

When examining these aggregation numbers, one thing becomes evident—the nonionic micelles and the anionic/nonionic mixed micelles can get very large. As Fig. 5 shows, aggregation numbers can easily be in the thousands. This would produce molecular weights in the millions for the aggregate micelle. This size could easily be removed by some microfiltration, and even more so by ultrafiltration.

A particular area for concern is the use of microfiltration with spray wash cleaners. Many of these cleaners are formulated with nonionics to minimize foaming. These are then typically used above their cloud point to further minimize foam generation. To operate a microfiltration unit in the region of 0.2 microns or less in this application would certainly appear to be an area where much surfactant removal could occur.

**Experimental Data**

Some work has been done within Modine Manufacturing Company, Racine, WI, to further test these concerns. A bench-scale pilot microfiltration system was built to run both new and used cleaner samples. The first indication that there might be surfactant removal appeared when evaluating the first trial run of the pilot system. Used cleaner was received from a manufacturing facility and tested per the EPA standard method for Oil and Grease.9

The gravimetric procedure involves acidification (pH<2) of the sample, then serially extracting it in a separatory funnel with Freon 113. The Freon fraction is then isolated and heated to evaporate the sample down to the non-volatile oil and grease residue. It can be expected that, when using the relatively polar solvent (Freon 113), much of the surfactant would be removed as well. For this reason, a virgin cleaner sample was tested along with the “before” and “after” filtration samples. The original intention was to use this as a “blank” to subtract from the results. Table 2 lists the results (without subtraction of the “blank”).

Note that the “used” cleaner had been used for a period of time, but was not considered to be “waste” cleaner in need of dumping. One could expect much higher numbers on a very old cleaning solution.

The results listed in Table 2 show the following:

- The virgin cleaner sample has a significant amount of “oil and grease.” Because there was no oil in the sample, this would have to be interpreted as surfactant only.
- The permeate samples show a lower “oil and grease” level than that of the new cleaner sample, indicating there has been some loss of surfactant (30% and 50%, respectively of the virgin cleaner that is Freon extractable).

It was then decided that more work would be required to isolate and confirm surfactant amount. The first step involved thin layer chromatography to determine what solvents would extract the surfactants present. It was determined that the surfactants could be isolated and quantified by infrared chromatography. Next, virgin cleaner was run through the pilot microfiltration system. Figure 6 shows percent loss of surfactant as a function of membrane porosity at room temperature. The percent of surfactant loss was nearly the same as the previous test.

Used cleaner was then run through the same porosity filters to determine efficiency of oil removal. This time, the test method involved a hexane extraction. This nonpolar solvent was effective in extracting the mineral-oil-based lubricant, while leaving most of the surfactant intact. Figure 7 shows the percent oil removal efficiency vs. filter porosity at 23 °C (73 °F). Figure 8 shows the same at 65 °C (150 °F).

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**Table 2**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oil &amp; Grease (ppm)</th>
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<tbody>
<tr>
<td>Used cleaner</td>
<td>336</td>
</tr>
<tr>
<td>Virgin cleaner</td>
<td>88</td>
</tr>
<tr>
<td>0.2 micron permeate</td>
<td>62</td>
</tr>
<tr>
<td>0.05 micron permeate</td>
<td>44</td>
</tr>
</tbody>
</table>
It should be noted that the 0.05 and the 0.2 micron permeate produced a very clear-looking solution. Porosities above this level produced gradually cloudier solutions. Also, an increase in temperature gave an increase in oil removal efficiency of 5–6 percent. This correlates with the surfactant theory presented earlier: That as the temperature increases, the size of the micelle increases, which would explain the increase in removal efficiency. Although it was not tested, it would be expected that surfactant loss would follow a similar trend, because one nonionic surfactant was present.

Additional testing has been done with other alkaline cleaners, confirming that these effects are not isolated to that cleaner alone. Other cleaners tested may not necessarily follow the same percentage of surfactant removal, although there is no doubt that surfactant loss is occurring.

**Minimizing the Effects**

Microfiltration has too much to offer from the standpoint of waste minimization and quality improvement to be ignored. A great deal of waste cleaner volume can be eliminated with this technology. Quality improvement is realized because the bath is maintained in a consistent state, minimizing the “sawtooth” effect of charging a fresh bath and watching its quality decline until it is ready to be dumped again.

Modine, therefore, set out to determine how it might best use this technology, given that surfactant removal is necessary to achieve good oil removal. Two paths were chosen:

1. To maximize oil removal efficiency while minimizing surfactant removal. Figure 9 illustrates this approach. Both surfactant remaining and oil removal curves are plotted vs. percent on the same graph. The point at which these two curves intersect is defined by the author as the optimal porosity. A membrane pore size should be chosen near to this optimal porosity.
2. To consolidate aqueous cleaners and focus on formulating the higher volume cleaners in-house. There are several advantages to this approach, of which the primary is control of the process tank. If Modine made the cleaner, it could test and rejuvenate it, if the surfactant removal appeared to be significant enough to have deleterious effects.

Another advantage was the removal of silicates from the cleaner. Sodium metasilicate will exist as a colloidal precipitate in solution and affect the membrane, causing blinding and plugging. The third advantage was the cost savings incurred by bringing this function in-house. Typical savings amounted to 40–50 percent.

**Conclusions**

Microfiltration appears to be the best technology available for the removal of emulsified oil from aqueous cleaning solutions. When used in conjunction with skimmers and coalescers, the useful life of these solutions can be greatly extended.

The mechanism by which microfiltration works will cause the removal of surfactants and possibly other components. The exclusion of emulsified oil by the membrane will at least cause the removal of the surfactants emulsifying that oil. Many cleaners will experience partial surfactant removal even without the presence of oil because of grouping of the surfactants in structures called micelles. Some of these micelles can be larger than the porosity of the membrane, which causes their removal.
Modine has been able to apply a number of disciplines to investigate this problem. A good deal more work can be done in these areas, though. Cleaner and surfactant manufacturers could stand to benefit from research in this area, particularly if done in conjunction with filter system manufacturers.

First, the parameters that cause surfactant removal need further investigation. How do the various conditions of an aqueous cleaner affect the micelle size? For what categories of surfactants are those conditions true? Do surfactants within these sub-groups behave the same or are there differences between individual surfactants?

Even the largest surfactant manufacturers have very limited data regarding micelle structure and size. The examination of these parameters is considered to be “academic” and, therefore, very little time or resources are devoted to its study. The parameters for the data that do exist are typically for conditions not similar to those found in an aqueous cleaner with regard to temperature, electrolyte, oil loading, etc. The surfactants they manufacture and sell could have more research into these other conditions to assist the cleaner manufacturers in their selection. Surfactant manufacturers could also focus energies on creating surfactants that form smaller or otherwise different micelle structures that could be more resistant to removal.

Cleaner manufacturers who ignore microfiltration because of the risk of lower sales volumes are not looking beyond the short term. Manufacturers willing to embrace this technology may not experience a downturn in business for two reasons. First, through establishing themselves as a leader in this field, they could find themselves building a larger customer base. Second, many businesses would likely be willing to pay a premium for a cleaner system that would allow them to go much longer between tank dumps. For both reasons, microfiltration could be a great benefit for those cleaner manufacturers that embrace this technology.

Other manufacturers who ignore microfiltration could experience a loss of business to those more skilled in the technology. History has shown that those willing to embrace new ideas have survived and even flourished in times of revolutionary change. This is such a time in the field of industrial cleaning, and those who ignore history are likely doomed to repeat it.

References

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