

# More from CAPS3: Surfactants, silicone-based solvents, and microemulsions

## A Surfeit of Surfactants

Back in the January 2009 issue of the *WAAC Newsletter* I did a piece entitled “Sorting Out Surfactants” which surveyed common surfactant products encountered in conservation and listed their various properties. Since then, the surfactant landscape has changed a little, and some new product types have emerged which are now starting to find their way into our field. What follows, then, is intended as a brief update to the 2009 article to highlight some of these new products and their possible applications in conservation.

We are probably all familiar with the non-ionic surfactant TRITON™<sup>1</sup> X-100 (also Synperonic N in the UK and EU) which has been something of a favorite of conservators everywhere. (It, along with propylene glycol, is also the active ingredient in Photo-Flo.)

TRITON X-100 is just one product in Dow’s range of TRITON X-series surfactants that are based on ethoxylated octylphenol. Two other products in that range, TRITON X-405 and X-305, have been and are probably still used in artists’ and commercial acrylic paints in the emulsion polymerization process and possibly also to aid pigment dispersion. X-100 has an average of 9.5 ethoxylate groups giving it a Hydrophile Lipophile Balance (HLB) number of 13.5 while X-405 has an average of 35 of the polar, hydrophilic ethoxylate groups increasing its HLB to 17.6.

These octyl- and nonylphenol based surfactants (also known as APEs, alkylphenol ethoxylates) are quite rough on the environment and are on their way out.

The surfactant itself is not the problem. The risk from these surfactants comes from the residual ethoxylated octyl- and nonylphenols, left when the ethoxylate groups degrade into ethanol molecules and float away. These molecules act as estrogen mimics, and as such have their effects at very low concentrations. The deleterious effects appear to occur at parts per billion ranges and lower so, it takes very little in the ecosystem to manifest problems in fish (or, potentially, people).

Octylphenol and nonylphenol cause feminization of male fish rendering them nearly sterile. (I suspect that it is not a coincidence that the common spermicide nonoxynol-9 is polyethoxylated nonylphenol.) Their discharge into the environment is, or is soon to be, prohibited in most countries.

TRITON XL-80N, an ethoxylated and propoxylated C8 - C10 alcohol, was released a number of years ago by Dow as an ecologically sound replacement for X-100. It was widely adopted by conservators, at least in the US. However, as does happen, XL-80N was then discontinued by Dow a few years ago. Another company, Huntsman, has released a very similar product Surfonic JL-80X that remains available. The Surfonic product is based on C10 - C12 alcohols rather than C8 - C10. You will notice in the table below that the properties of JL-80X are not quite identical to XL-80N.

Because of the environmental problems associated with alkylphenol ethoxylates, manufacturers are now producing ranges of alternative non-ionics including those that are readily biodegradable without harmful effects, so as to be nicer to any creatures downstream from our work sites, piscine and otherwise.

The one that we’ll discuss here, offered by Dow under the ECOSURF™<sup>1</sup> brand, is the ECOSURF EH series (EH-3, EH-6, and EH-9) which are based on an ethoxylated/propoxylated branched alcohol (2-ethyl hexanol) rather than the straight chain alcohols found in TRITON XL-80N and Surfonic JL-80X.

These surfactants dissolve well in both water and low polarity solvents so they can be cleared (rinsed) with either water or low polarity solvents, giving a lot of flexibility in their use. Dow’s tests, as reported in their literature, show that they are generally more effective than the linear alcohol ethoxylates and compare well with the nonylphenyl ethoxylates, at least when it comes to greasy soils and cross-linked baked-on soils.

ECOSURF products have featured in the continuing joint research project between Dow, GCI, and Tate that aims towards improved materials for the cleaning of acrylic paint, and some of them were tested at CAPS3 (as described in the preceding review of the workshop). And the ECOSURF EH series (EH-3, EH-6, and EH-9) have now been added to the MCP, which most of the world won’t see until the next update of the program.

<sup>1</sup> Trademark of The Dow Chemical Company (“Dow”) or an affiliated company of Dow.

Table 1  
Physical properties  
of selected nonionic  
surfactants

Common Name	CAS number	cmc	Density	HLB	Cloud Point	MW
Ecosurf EH-3	64366-70-7	0.0480	0.9651	7.9	52	NA
Ecosurf EH-6	64366-70-7	0.0914	1.0022	10.8	43	NA
Ecosurf EH-9	64366-70-7	0.1066	1.0237	12.5	61	NA
Laureth-3 POE	3055-94-5	0.175	0.9222	7.8	37	341
Triton X-100	9002-93-1	0.015	1.07	13.4	66	628
Surfonic JL-80X	68154-97-2	0.00885	1.0072	13.1		603
Triton XL-80N	68603-25-8	0.0086	0.985	12.5	50	442

Exploiting their solubility in low polarity solvents, all three products were dissolved in mineral spirits and found some effective uses in removing materials from sensitive acrylic surfaces. I suspect that the polar ethoxylate/propoxylate chains were drawing the more polar components into the mineral spirits though hydrogen bonding.

But the real fun comes when you add some other new things into the mix.

### Microemulsions and ECOSURF EH-3

Dow, Tate, and the GCI introduced microemulsions to the conservation profession at the 2009 Los Angeles AIC Meeting. More recently, Richard Wolbers has been working on a new class of microemulsions for cleaning. He developed them for cleaning acrylics, but I think they will find incredibly wide use in the broader world of conservation.

There is much that is new to the conservator in these systems. First, they are microemulsions (microemulsions will be discussed shortly). Second, they are made with silicone-based solvents. What makes them particularly versatile is that the water content can be varied from 10 to almost 50%.

The very word “microemulsion” is likely new to many conservators, and it is more than the name implies. A microemulsion, you might think, is just an emulsion with smaller droplets. And you would be partially correct. But a microemulsion is not just a regular emulsion beaten with a hammer, or otherwise forced to form smaller micelles.

Given the right conditions, a microemulsion forms spontaneously – they actually require less shaking and cursing than a conventional emulsion. The trick to making a microemulsion is to adjust the properties of the solvent, water, and surfactant so that the solvent/surfactant and the water/surfactant have the same or nearly the same surface energy. (Often a cosol-

vent has to be added, typically a long chain alcohol, to get the surface energies to be compatible.) The two phases should spontaneously form a water in oil, an oil in water, or even a lamellar emulsion depending on the relative proportions of solvent to water.

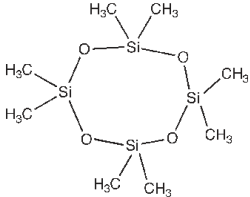
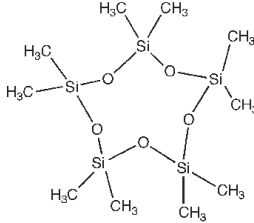
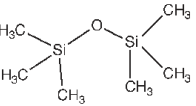
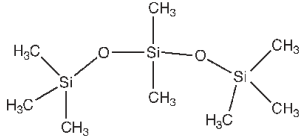
An oil in water emulsion, micro- or otherwise, has the oil phase in the small spherical micelles studded by surfactant molecules. In a water in oil emulsion the micelles are filled with the aqueous phase and the dispersed phase is the oil (solvent). A lamellar emulsion is smack dab in the middle of the o/w and w/o emulsion types. Rather than forming spheres, the water phase and the oil phase each form layers separated by layers of surfactant. It’s rather like the layers in puff pastry, a thin layer of pastry, a layer of butter, a layer of air, a layer of butter, a layer of pastry, repeat...

And, not surprisingly, the droplets of the dispersed phase in a microemulsion are much smaller than those of a conventional emulsion. They are so small, in fact, that they don’t scatter light, so a microemulsion is not creamy white but transparent.

The smallness of the micelles also allows for the emulsion to have a low viscosity. The emulsion viscosity can be increased, if one chooses, by changing proportions of materials. When conditions are changed to shift towards the formation of the lamellar microemulsion structure mentioned above, the solution viscosity increases.

The solvents used to form these microemulsions will also be new to most conservators. Silicone-based solvents or VMS (volatile methoxysilanes) are a class of unbelievably low polarity materials. They reside at the low end of the spectrum of polymerized dimethylsiloxanes. The smallest is the dimer, hexamethyldisiloxane which is a fast evaporating solvent. The high end of the range of the polymer family is silicone rubber and between the two extremes are the silicone oils and silicone gels (of breast implant fame).

Table 2 Introducing the silicone-based solvents: their names and faces.

Name	Cyclomethicone D4	Cyclomethicone D5
Chemical Name	octamethylcyclotetrasiloxane	decamethylpentaoxapentasiloxane
CAS	556-67-2	541-02-6
BP	172	210
MW	296	370.77
		
Name	Hexamethyldisiloxane	Octamethyltrisiloxane
Chemical Name	hexamethyldisiloxane	octamethyltrisiloxane
CAS	101	152
BP	162.38	236.54
MW		
		

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A notable characteristic of these solvents is that they feel greasy! And when you play with them, they will also feel familiar. This is because so many personal care and cosmetic products have silicone solvents in their formulation. Skin creams often contain either a silicone oil, gel, or a non-silicone material that leaves a greasy film behind. While our everyday experience with these products leaves us tempted to assume that these solvents will leave a greasy splotch behind, they will not. (You can easily verify this by placing some on a clean glass surface and looking for residue after the solvent evaporates. You won't find any.)

The silicone solvents also have no surface tension. They will spread out to a surprising amount on a surface. This may also take some getting used to when working with them.

The groups of interest to conservators are the short chain solvents and two cyclic structures, the cyclomethicones D5 (decamethylpentacyclosiloxane) and D4 (octamethyltetra-cyclosiloxane). (The cyclomethicones are often obtained and used in a mixed isomer product that is much cheaper than either pure D4 or D5.) In addition to very low solvent polarity, they have nearly no odor and evaporate relatively slowly. The solvents are considered relatively safe via inhalation from a health and safety perspective, but should, of course, be used with adequate ventilation or appropriate personal protective equipment.

So, why a microemulsion and why one with a silicone-based solvent?

Well, very often we want to pick up a water soluble material which is sitting on a water sensitive surface. In really bad cases, it is clinging or has even insinuated itself into the surface. If we can disperse small spheres of water in a nonpolar solvent, we can have our cake and eat it too. The flood of non-interacting solvent keeps the sensitive surface under control, while the small spheres of emulsified water can pick up the grime while only minimally affecting the surface.

A microemulsion gives us additional advantages over a conventional emulsion. First, it is transparent and we can see what is happening as it functions, distinctly different from watching a puddle of milky emulsion sitting on a surface and crossing our fingers. Equally important, microemulsions are not as prone to breaking. Often a conventional emulsion will break, separate into two phases, when the composition of the aqueous phase changes as material is being dissolved. (This is probably caused by a change in ionic strength of the dispersed water phase that disrupts the finely tuned balance between the surfactant, the water phase, and the continuous phase of the emulsion.)

Richard has made a phase diagram that describes the properties of mixtures of cyclomethicone D4, laureth-3 POE (L-3) surfactant, and water. We found at the CAPS3 workshop that ECOSURF EH-3 works better than the L-3 at building the microemulsions. (Better in this case means that the emulsions with the L-3 and the EH-3 both formed all of the the microemulsions we tested but the EH-3 –built microemulsions were a little clearer and “prettier” than the L-3 ones.) So I've

copied his diagram but changed the surfactant to EH-3 to try to make things a little less confusing. (See Figure 1.)

Another extraordinary feature of this particular microemulsion system is that the aqueous phase can have a fairly high ionic content and not adversely affect the emulsion. (Remember how conventional emulsions often “break” when they pick up too much ionic material, i.e., dirt.) This allows one to make all sorts of adjustments to the aqueous phase – varying the pH, raising or lowering the conductivity, and choosing specific ionic materials to incorporate, as well as other ‘actives’ like chelating agents, etc..

The phase diagram represents how different proportions of the components will form different types of emulsions. The circles in the shaded zone represent microemulsions, the triangles are conventional water-in-oil emulsion, the squares are conventional oil -in-water emulsion. The remaining areas show where oil and water don't mix. Note that all percentages are by weight.

Within the microemulsion phase, Richard has described a number of specific mixtures (Table 3). Of particular interest, note that the aqueous phase can range from 10% to nearly 50%. This gives us a huge range of aqueous activity with which to experiment. Especially considering that we can also manipulate the aqueous phase to be more or less aggressive to the grime by varying the pH or adding chelating agents.

To mix these microemulsions, I use small vials (obtained from DiscountVials.com) and a small scale (see Technical Exchange in the last *WAAC Newsletter*) and dispense the materials to be weighted directly into the vials. I make 10 gram batches, so I just divide the percentages above by 10 to get the weight of each material to add. You will probably not be surprised to find that I use the MCP to make the aqueous phase, setting the pH with a buffer, possibly adding an ionic buffer and/or chelating agent. The cap is screwed onto the vial and, after a quick shake, you should have a clear (or sometimes nearly clear) microemulsion. The viscosity of the emulsions vary; some are water thin while others are somewhat gelled.

The microemulsions are cleared from the surface with more silicone solvent. The cyclomethicone can certainly be used for this but it evaporates quite slowly. I prefer to use the hexamethyldisiloxane for rinsing as it evaporates quickly, comparable to a fast evaporating mineral spirits.

At the risk of being redundant, I think the combination of the ultra-low polarity silicone solvents, the relatively wide range of water concentrations, and the capacity to load buffers and chelators into the aqueous phase makes the systems described above incredibly promising for removing grime from water sensitive surfaces.

In fact, in my opinion, when approaching the cleaning of an acrylic paint surface, we will first try silicone microemulsions (varying the properties and amounts of the water phase), then aqueous cleaning systems tailored to minimize swelling by controlling the pH, ionic strength, additional ions, and osmotic effects, realizing that this will affect the paint more

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Figure 1

Richard's phase diagram for mixtures of surfactant, solvent and water showing the area where a microemulsion phase will form.

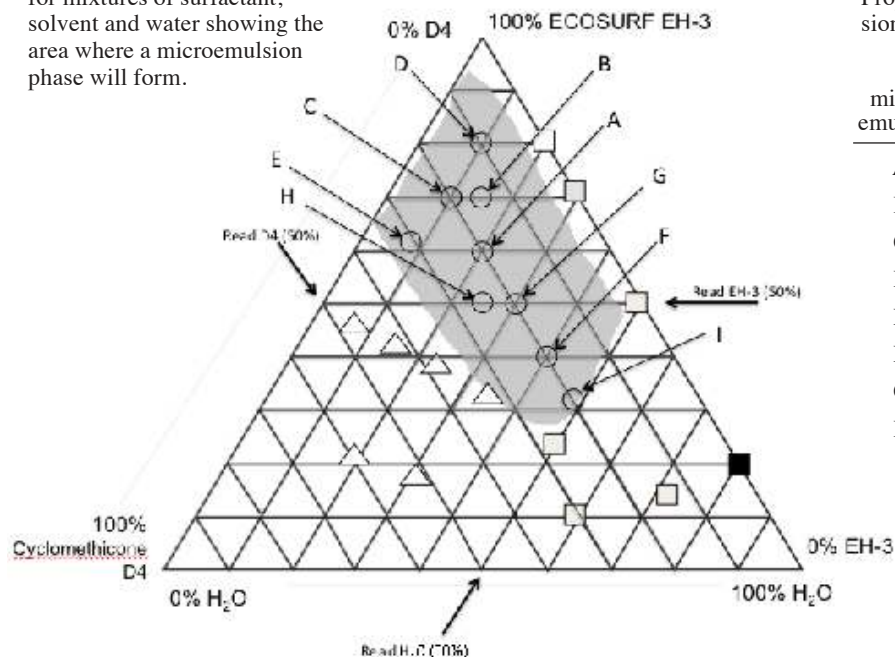


Table 3

Proportions (by weight) of the microemulsions indicated in Figure 1.

micro-emulsion	% cyclo-methicone	% surfactant	% water
A	20	60	20
B	15	70	15
C	20	70	10
D	10	80	10
E	30	60	10
F	20	40	40
G	20	50	30
H	50	25	25
I	20	30	50-ish

than the emulsion. If this still will not do the job, I think we will then reach for systems to swell the acrylic just enough to unlock engrained dirt. An aqueous Pemulen TR-2 gel at pH 6.5, possibly with mineral spirits emulsified in would represent the big guns. Again, this is just my opinion and subject to change as research proceeds.

### More microemulsion madness

The foregoing is by no means the only work being done with microemulsions, so I'll finish with a summary of some ideas in development.

The Dow/Tate/GCI collaboration has developed and tested a number of water-in-oil microemulsion systems based on aliphatic hydrocarbon solvents.

Three classes of microemulsions have been experimented with, all using High Throughput (HTP) automated testing at Dow and by conservators. The first systems I saw were incorporated into CAPS2 at MoMA in 2011. These were based on Shellsol D38, the anionic surfactant linear alkyl benzene sulfonate (LAS), and water with a blend of butanol and hexanol as the cosolvent. The water varied from 34% to 70%. These were a bit too effective although they have been used by some for removing very ingrained soiling from acrylic grounds.

For CAPS3, the second generation of microemulsions born from the HTP research was introduced. These microemulsions were formulated with Shellsol D38 (or Alcosol D40 in the UK), nonionic ECOSURF EH-6 as the surfactant, water, and mixtures of butanol and hexanol as the cosolvent. The water phase was 8-9%; these were found to be much better

behaved on the more fragile acrylic paint samples, working more slowly and controllably.

A third series of microemulsions based on the anionic branched sulfosuccinate surfactant TRITON™ GR-7M is being evaluated in comparison with the first two generation microemulsions by Bronwyn Ormsby and the conservators at the Tate.

I look forward to the forthcoming release of the phase diagrams and cleaning performance evaluations of these novel cleaning systems from the Dow/Tate/GCI collaboration. I promise to cover these and other microemulsion developments in a future *WAAC Newsletter*.

And, as well, Richard also had a few microemulsions based on mineral spirits, TRITON XL-80N, and water that he persented at CAPS3. The aqueous phase varied from 10-30% and the XL-80N was used at 30%.

Supplies: Pure VMS solvents can be obtained from Shepard Bros. in La Habra, CA, contact Scott Hudnall (scott\_hudnall@shepardbros.com). Much less expensive mixed isomer D4 and D5 cyclomethicone can be ordered from The Chemistry Store.com. By the time you read this, the ECOSURF EH line (EH-3, EH-6, and EH-9) should be available from Conservation Resources International. L3 can be obtained (in bulk) from www.makingcosmetics.com.

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