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Editor's Note: This article is reprinted from the March 2008 issue of TLT.

When oil and water do mix

Thanks to the fascinating world of surface chemistry, you might have more options than you think when it comes to combining fluids.

KEY CONCEPTS

- There are several materials that derive some or all of their properties from the use of surfactants.
- The physical and chemical behavior of liquids cannot be understood without taking surface tension into account.
- The difference between suspensions, dispersions and emulsions is their inherent stability or tendency not to separate or settle.

According to conventional wisdom, oil and water don't mix. While most oils and waters have some very minute solubility in each other (on a macro scale, for example), you really can't mix the two to get a true solution.

I remember the old DuPont adage: "Better living through chemistry." Both Mother Nature and Mankind have shown admirable skills in this regard. What I'm referring to, of course, is the wonderful and fascinating world of surface chemistry.

As tribologists we are concerned very much with certain aspects of surface chemistry such as wear processes, tribochemical reactions, friction, etc.—the whole nanoworld where certain atoms or molecules on surfaces come in contact with other chemicals to produce interesting results. In the case

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of oil and water, I'm referring to the chemistry of surfactants or surface-active agents. Surface-active agents allow us to mix incompatible materials in a generally synergistic manner for some purpose.

There are all kinds of materials around us that derive some or all of their properties from the use of surfactants, including engine oils, metalworking fluids, certain lubricants, face creams, lotions, conditioners and cosmetics, shaving cream, water-based paints and coatings and food products conjured by man.

We all know chemical companies can do some pretty amazing things, but what about Mother Nature? One example that we encounter virtually at birth is obviously the most common and best formulated: mammalian milk.

To understand all of this, we first need to review the following definitions and, yes, I know there is a bit to digest here.

PROPERTIES OF SURFACE CHEMISTRY

1. **Wetting.** The spreading and penetrating properties of a liquid caused by lowering its surface tension—that is, the tendency of its molecules to adhere to each other.

2. **Suspension.** The condition of a substance whose particles are dispersed through a fluid but not dissolved in it; the condition of one having relatively large particles that will separate on standing. These are materials that always say, "shake well before using" on labels. In nature, a muddy river might be an example—once it stops flowing, the mud settles and the water is clear again.

3. **Colloid.** A solid, liquid or gaseous substance made up of very small, insoluble particles (as single large molecules or masses of smaller molecules) that remain in suspension in a surrounding solid, liquid or gaseous medium of different matter. Colloids usually are pretty stable; thus a stable colloidal suspension such as milk consists of an immiscible liquid (butter fat) dispersed and held in another liquid by substances called emulsifiers.

4. **Dispersion.** A colloidal system with its dispersed particles and the medium in which these are suspended. These are materials that sort of fit in the middle. Most dispersions need or should be shaken or stirred before use. Some salad dressings immediately come to mind.

5. **Surface Tension.** The effect within the surface layer of a liquid that causes the layer to behave as an elastic sheet. Surface tension allows insects to walk on water. It also allows small metal objects such as needles, razor blades or foil fragments to float on water, causing capillary action. Whenever a rain drop falls or a cleaning agent is mixed with water or an alcoholic beverage is stirred in a glass, the effects of surface tension are readily visible. Everyone is familiar with water droplets forming large beads (because of water's high surface tension ~72) on a waxed surface (low surface tension ~<22), like a clean, freshly waxed automobile hood. The physical and chemical behavior

of liquids cannot be understood without taking surface tension into account. It governs the shape that small masses of liquid can assume and *the degree of contact a liquid can make with another substance.*

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6. **Surfactant.** A substance such as an emulsifier, detergent or wetting agent that lowers the surface tension of the solvent in which it is dissolved or *the tension at the interface between two immiscible liquids.* Add just a little soap to the water in the example above, and the water no longer beads on the car hood but forms a smooth sheet.

OPTIONS

Okay, let's try to cut to the chase. If we want to mix oil and water, we can do a poor job by making a suspension, which depends on the nature of the oil or maybe by just shaking it up a lot so it will be stable for a little while. In addition, we can make a dispersion by adding a surfactant and stirring or shaking (mixing with a fair amount of energy). In addition, we can make an emulsion with a different surfactant (a better one for our particular system—an emulsifier), mixed with energy, resulting in a stable emulsion. So with a little magic, we have mixed oil and water.

Now let's strip away the alchemist's robes, cowl, incantations and crow feathers and look at what's going on. First, the surfactant is a molecule that typically has a long carbon chain tail with some kind of polar head attached, as shown in Figure 1. You can think of it as kind of like a piece of spaghetti with something very different from pasta on the end of it.

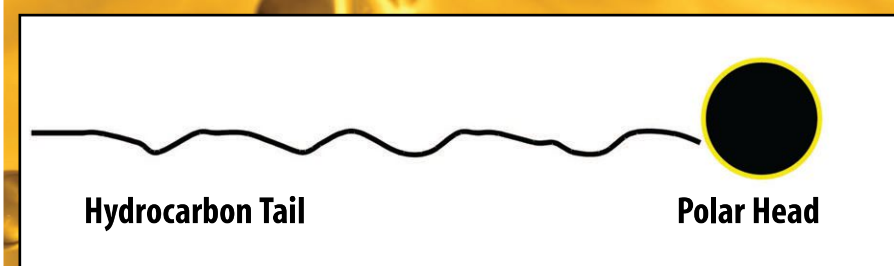

Figure 1

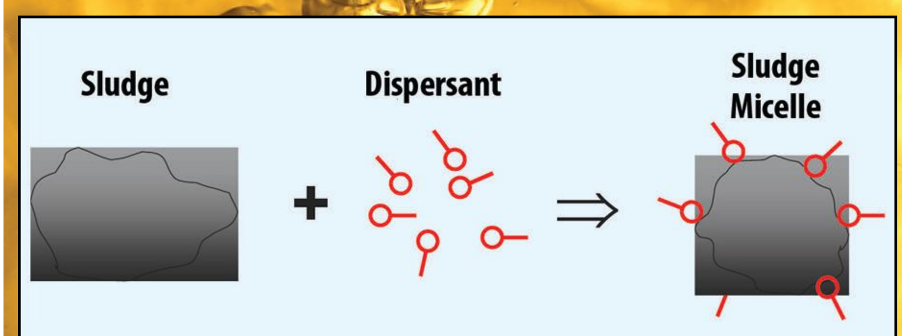

Figure 2

The polar head generally likes polar solvents such as water, while the hydrocarbon tail generally likes nonpolar solvents such as oil or other similarly long, straight-chain nonpolar chemicals. Polar solvents and functional groups on molecules generally have some kind of ionic character: plus or minus charges, partial plus or minus charges or just atoms with a lot of loosely held electrons.

The polar heads of the surfactant like water; they align themselves like a ball in the water with the polar heads on the outside (because they like water) and the long nonpolar tails to the inside (because they don't like water). These structures are called micelles. In nonpolar solvents, they do just the reverse; that is, the polar heads align to the interior of the ball and the nonpolar tail to the outside.

OK, so what does this have to do with mixing oil and water? Well, in a polar solvent the oil would be happiest in the center of the micelle because the long straight carbon chains are like the oil molecules. Conversely, if we had only a little water in our oil, the micelle would reverse and the water would move to the interior of the micelle. When this happens to the micelle in a chemical system, we call it an inversion. While these descriptions are a little simplistic, a polar material is made more or less compatible with a nonpolar material. The following are some visual examples that might make this easier to understand.

For example, imagine motor oil with a dispersant. The engine dirt tends to be polar, so the polar heads of the dispersant attach to the polar parts of the dirt to keep it in suspension in the oil until its time for an oil change or the particles agglomerate to a large

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enough size to catch in the oil filter (*see Figure 2*).

As shown in Figure 3, imagine very polar calcium carbonate ($CaCO_3$ with positive charges on calcium) dispersed in a nonpolar solvent like oil, hexane, etc., and containing a dispersant that has a polar sulfonate head (SO_3- with a minus charge). Thus, the nonpolar tails are to the outside of the micelle, making the calcium carbonate compatible with the nonpolar solvent. Hopefully, you'll see a pattern begins to emerge.

One of the key things that characterize the difference between suspensions, dispersions and emulsions is their inherent stability or tendency not to separate or settle. Aside from the relative goodness of the surfactant, the most important part is the particle size (whether gases, solids or liquids) of the material being dispersed. They settle because the particle size is too large and/or not enough surfactant is on the surface to keep them from settling.

In emulsions, the particle sizes tend to be quite small, usually well less that you can see with dispersions being larger and suspensions very large, indeed. To make an emulsion, sometimes you must have vigorous mixing or even milling or grinding to get the particle size small enough (because small particles have more surface area relative to their mass than larger particles) to get enough surfactant on the surface to do the job.

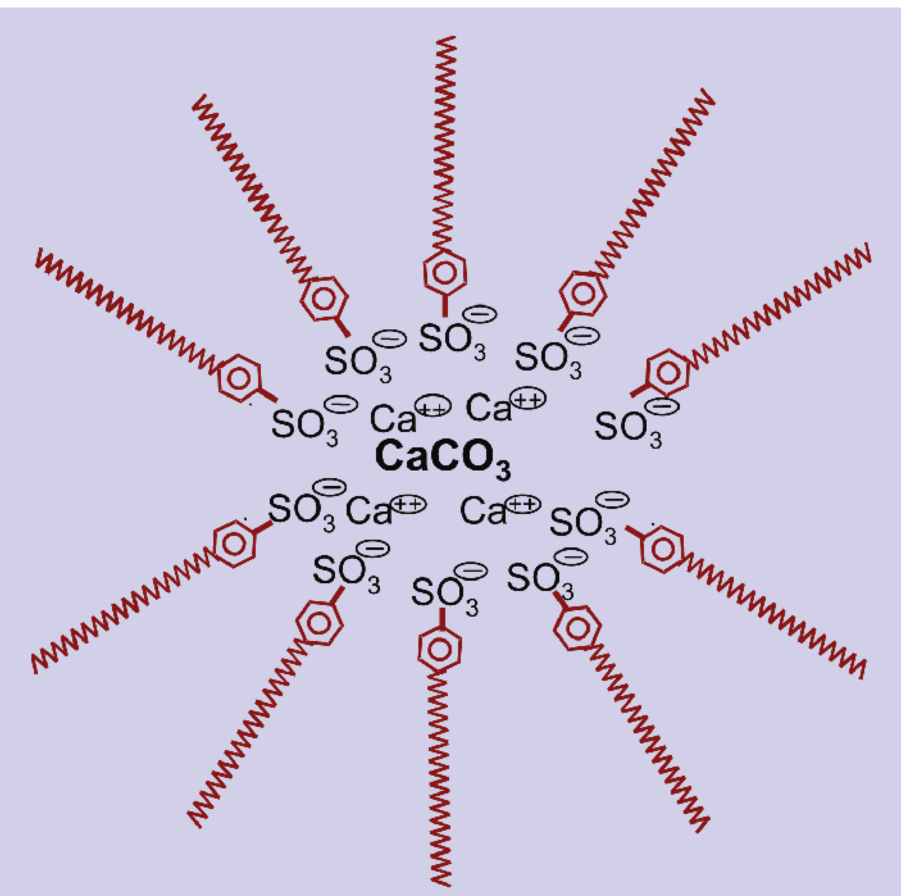

Figure 3

As a further example, back in those thrilling days of yesteryear when I was a young chemist, I developed a process for a particular chemical. The final step in the process resulted in the chemical precipitating (coming out of solution) into a nice crystalline slurry form that could be filtered like beach sand from the reaction mass, dried and sold as a final product. When I scaled it up in the plant to 5,000 gallons, low and behold, instead of a slurry I got something that looked more like a giant beer head containing my product.

Alas, I couldn't pump it to the filter, as the kettle drain was on the bottom and the beer head would hang up in the kettle and plug the drain. "It didn't happen like that in the lab!" Ever hear that one before? I was lower than a snake's belly in a wagon rut. Oh, woe, what to do? Enter the MPS (Magic Pinch of Stuff), in this case a product called Trition100X. I don't know if it is still on the market, but it either is or was an excellent surfactant. Anyway, I added an ounce to the kettle and Shazam! I got my slurry of beach sand and off to the filter we went.

What happened? The solids entrained small air bubbles from the more vigorous mixing in the bigger kettle and the differences in surface tension between my product and the reaction mass. The solids did not wet out but, rather, had tiny air bubbles coating each crystal, causing them to float. The addition of the surfactant caused the surface tension to change at the surface of the solids, the foam broke immediately, the slurry returned and my job was secured until the next crisis.

In one of our case histories in STLE's Metalworking Fluid Management Certificate education course, we have a similar example where metal fines are floating in a metalworking central system with the lack of wetting being the problem. To carry the previous story a little further, Triton 100X (I have to use the trade name because I have forgotten the chemistry) could be used in higher concentrations as a dispersant or emulsifier or, in much higher concentrations, as I understand it, to make a stable foam for shaving cream. A great MPS!

So now you know how to mix oil and water! That was the prime purpose of this article, and if this information is all you are interested in you can stop reading here. But if you want extra credit, read on.

What do you do if you *don't* want to mix oil and water—that is, you don't want a stable emulsion? Ask your Mom. When she runs out of buttermilk and can't get to the store, she takes regular whole milk, adds a little vinegar, stirs it up and presto—she has buttermilk! What she did was break Mother Nature's emulsion by adding acid, which ties up the polar heads of Mother Nature's surfactant, and the butter drops out in globs.

The better the emulsion, the longer the fluid lasts in the system and the happier the customer.

Many MWFs are emulsions. The better the emulsion, the longer the fluid lasts in the system and the happier the customer. But eventually it is time to finally send the fluid to the waste treatment system. What happens?

Well, a really good emulsion just might go through the waste treatment plant (depending on its design) and out into the waste stream. Not good! So the waste treatment manager treats the emulsion with acid, the emulsion breaks and then the waste system can capture and concentrate the waste, leaving the waste stream to the environment clean.

So if you want to mix oil and water—no problem. And if you don't want to mix oil and water—no problem. Like DuPont says, "Better living through chemistry!" TLT

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