Welcome to Version 11 of the MCP – Microemulsions and Dewetting
(or The Hitchhiker's Guide to the Universe of Dewetting)

by Chris Stavroudis

Without too much fear of contradiction, nano-structured fluids are the next development in cleaning systems in conservation. Giving credit where credit is due, I like to refer to them as Baglioni-style microemulsions.

Dr. Piero Baglioni and his coworkers at the Center for Colloid and Nanoscence (CSGI) at the University of Florence have developed and popularized these systems though workshops, lectures, and articles. They have been leading the advancement of these cleaning systems in the field of conservation, and many of their published formulations are included in the new version of the MCP. Their cleaning systems have introduced the conservation profession to the concept of dewetting, a term and concept which is new to most of us.

So, before discussing Baglioni-style microemulsions and the MCP, a simple description of dewetting.

Dewetting is a complex phenomenon consisting of several steps that result in the detachment of the polymer film from a substrate.

In short, in the dewetting process, the microemulsion reduces the adhesion of the coating to the substrate.

It achieves this by creating an environment in which the coating has greater affinity for itself than the substrate. The net effect is the film swells and releases from the substrate, allowing it to be pushed off the surface.

In actual application, one interesting aspect is that dry media tools (cotton, scalpel, bamboo stick, dental tool, plastic scraper) are often more effective to push off or lift the swollen film from the substrate. Using a swab dampened with the microemulsion system to push or roll the detached film tends cause it to stick to the surface. In cases of partial dewetting, a swab lightly dampened with pH adjusted water, Shellsol D-38, or cyclomethicone D5 can be used to slightly lubricate the surface and push the film off without swelling it.

The MCP Way

Before proceeding to microemulsions in the MCP, it is important to note that there are some differences between the Baglioni system and the MCP.

One of the foundations upon which the Modular Cleaning Program is built is the control of the pH of cleaning systems.

Where his group builds their microemulsions with distilled water, we tailor our aqueous phase to each surface with an appropriate buffer. For instance, to solubilize acidic soiling materials we control the pH of the continuous phase at a higher pH, while simultaneously swelling the coating. And because one of the initial stages of dewetting is swelling, it's a win-win.

For substrates that require a lower pH, it's as simple as choosing one of the standard MCP buffers with a lower pH range – just as you normally would.

We also know that a surface can be embedded or intermixed with grimy components that require a chelating agent to remove them. Removal facilitates greater interaction between the microemulsion and the coating. This is addressed in the MCP by enabling the addition of different chelators into the aqueous phase of the microemulsion.

The CSGI microemulsions were initially designed for removing ill-considered coatings from fresco surfaces. There, you would want to avoid chelating agents to prevent the solubilization of calcium ions, and any attempt at control of pH would be overwhelmed by the inherent pH of the substrate.

Considering the microemulsion they designed for removing an acrylic coating from a Pollock at the Peggy Guggenheim Museum in Venice, the coating would have been clean enough that a chelator would have been unnecessary. And, being synthetic, would not have oxidized, so pH control would be a moot consideration.

Microemulsions

After the articles that have appeared in the *WAAC Newsletter*, you all should know that having and maintaining the proper proportions in a microemulsion is critical to the cleaning system. The difference between having a microemulsion, a conventional emulsion, or a layer of oil (solvent) floating on a layer of water lies in the proper amounts of the components assembled in the correct order. When the microemulsion is mixed with the correct percentages (by weight), the microemulsion will form spontaneously with a gentle stir or shake.

So how do we reconcile this system which requires precise proportions of the components with the desire to control the pH and include a chelator.

The solution is to create MCP component solutions so concentrated that they don't disturb the microemulsion balance.

Here enters Luke Addington and the concept that we are calling Ultra-Concentrate solutions – MCP solutions so concentrated that a drop or two can change the pH of or add a chelator to the system at the appropriate concentration while maintaining a stable microemulsion.

The answer to the **ultimate question of life, the universe, and everything** is not 42[1] but rather 62.5. That is the magic concentration multiplier which will be used for the Ultra-Concentrate solutions.

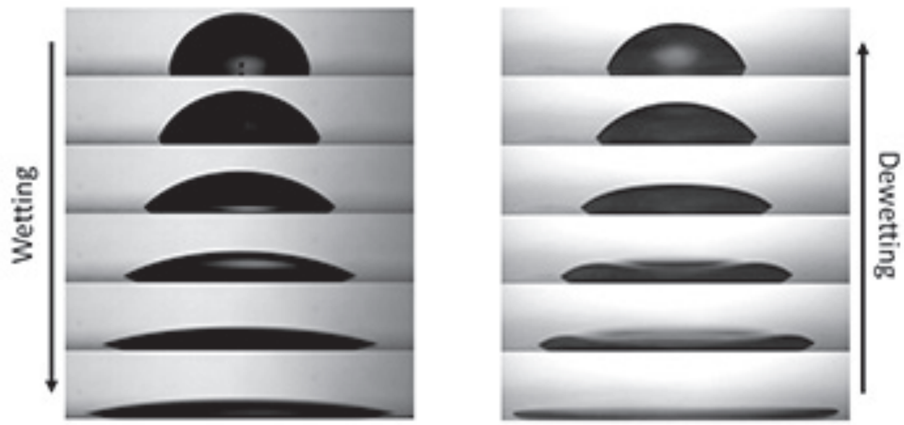
1. Adams, Douglas. 1979. *Hitchhiker's Guide to the Galaxy.*

Some Notes on Dewetting

Dewetting

In fluid mechanics, dewetting is one of the processes that can occur at a solid–liquid, solid-solid or liquid–liquid interface. Generally, dewetting describes the process of retraction of a fluid from a non-wettable surface it was forced to cover. The opposite process—spreading of a liquid on a substrate—is called wetting

(wikipedia)



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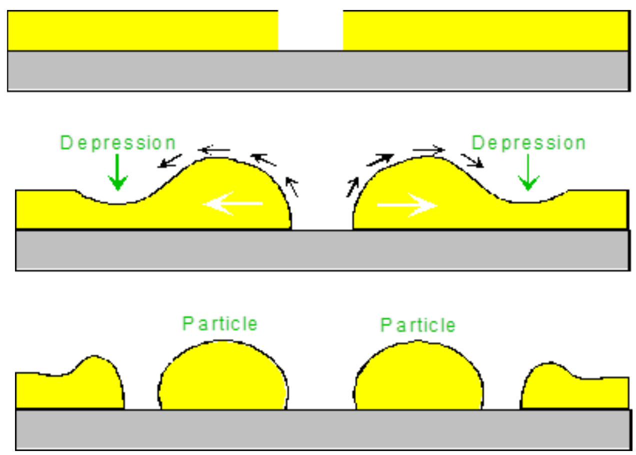


Solid State Thermodynamics Lab, Israel Institute of Tehnology

Dewetting II

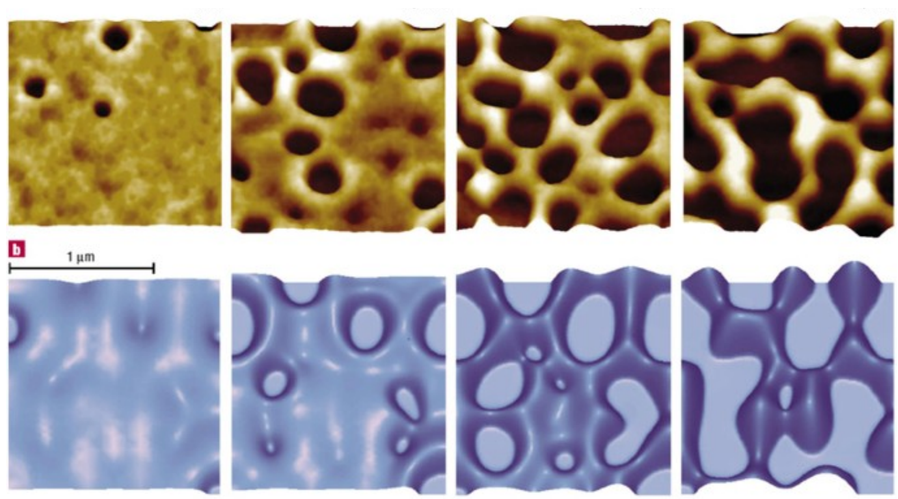
Dewetting is the hyrodynamic process where a uniform layer of liquid destabilizes and decays into distinct patterns of stationary droplets by virtue of interfacial and intermolecular energies.

(Signatures of slip in dewetting polymer films. Peschka et al.Proceedings of the National Academy of Sciences, May 2019, 116 (19) 9275-9284)

Can be used to remove polyer coatings from artwork substrate.

Dewetting III

With a properly designed o/w microemulsion we can swell a polymer layer causing the Tg to decrease. This plasticizes the polymer allowing the chains to move more freely in the film. The surface energy of the film, in contrast to that of the substrate (and water continuous phase) increases. The polymer layer goes though a number of stages and ultimately spontaneously pulls away from the substrate – it dewets.



Nature Materials

The normal/traditional/original/classic/legacy MCP solutions are concentrated 5x. That is the reason for the mantra "one plus one plus one plus one plus one equals five." The working concentration of buffers and chelators used in the MCP is 0.05 M. So, the normal/traditional/original/classic/legacy solution concentrates are 0.25 M.

The Ultra-Concentrates are at 3.125 M.

Rather than using 1 ml of the concentrate solutions we will use 1 ml distilled or deionized water and add to that roughly 2 drops of the Ultra-Concentrate solutions.

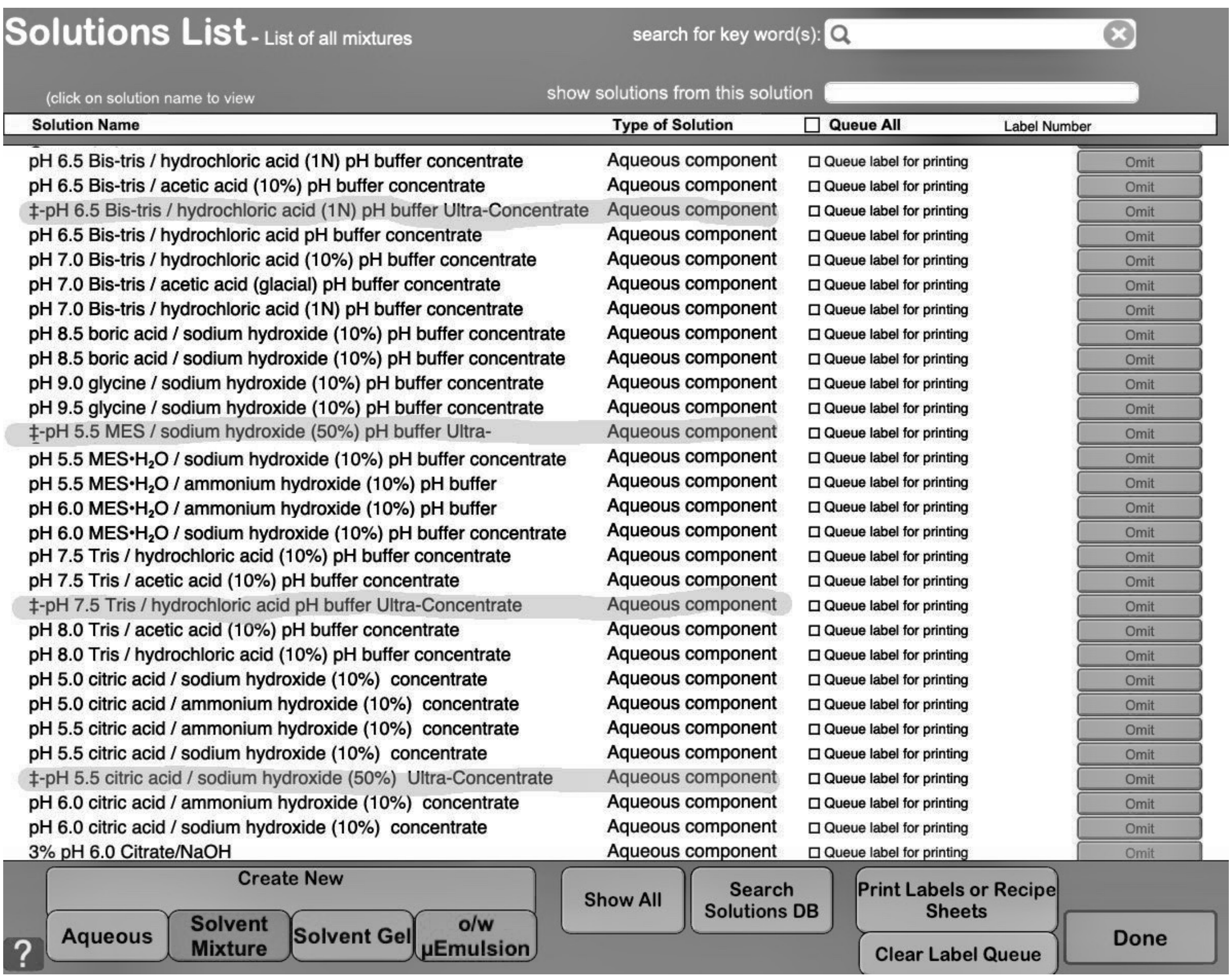
Rather than mixing 100 ml of the concentrate solutions for our testing kits, the new system will consist of small vials of 10 ml Ultra-Concentrate solutions. The Ultra-Concentrate names will all be distinguished by the double-dagger (‡).

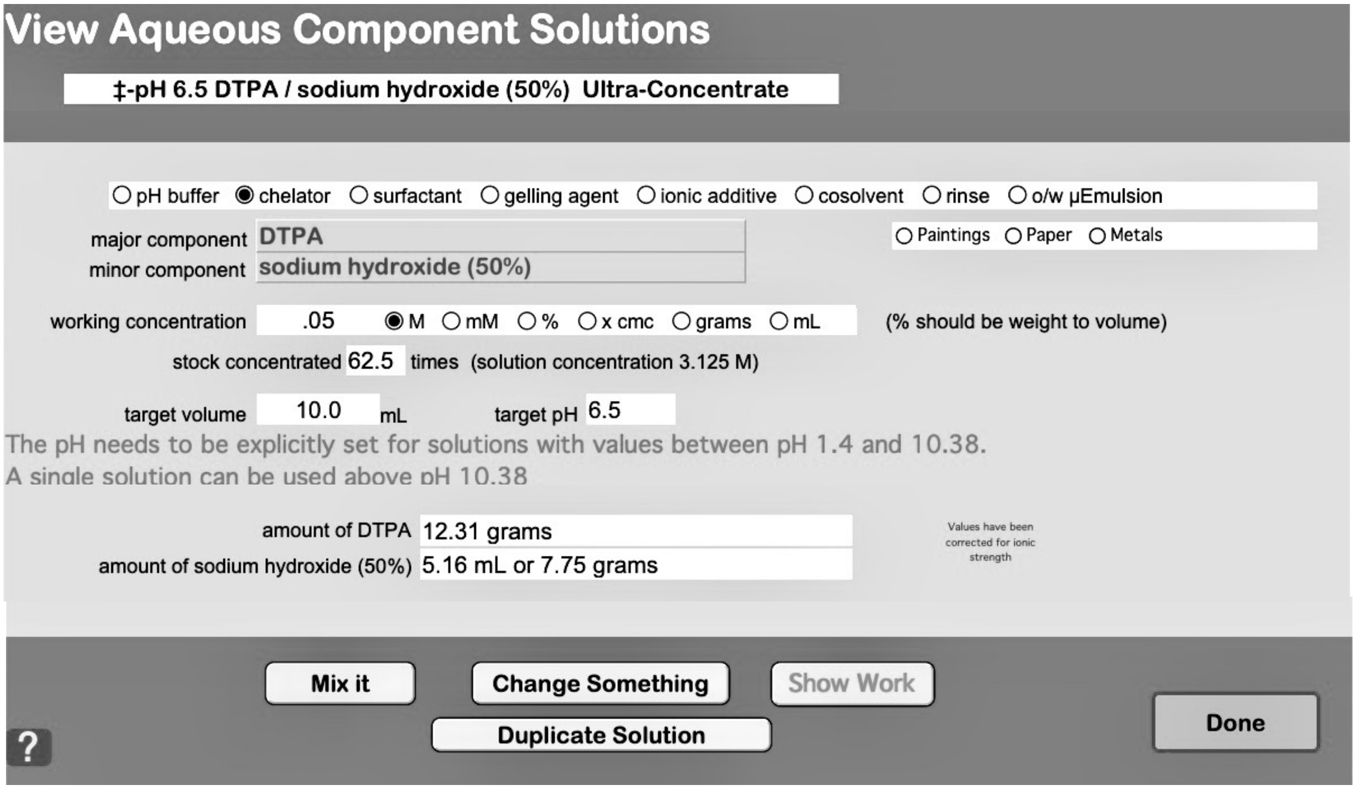
Want to set the pH of 5 ml of a stock microemulsion built with distilled/deionized water to pH 5.5? Add 2 drops of pH 5.5 Ultra-Concentrate buffer solution. Simple and elegant (and I'm so jealous that I didn't think of it).

This is how the Solutions Database looks with the Ultra-Concentrate stock solutions included in the listing:

The grey highlights are the new Ultra-Concentrates.

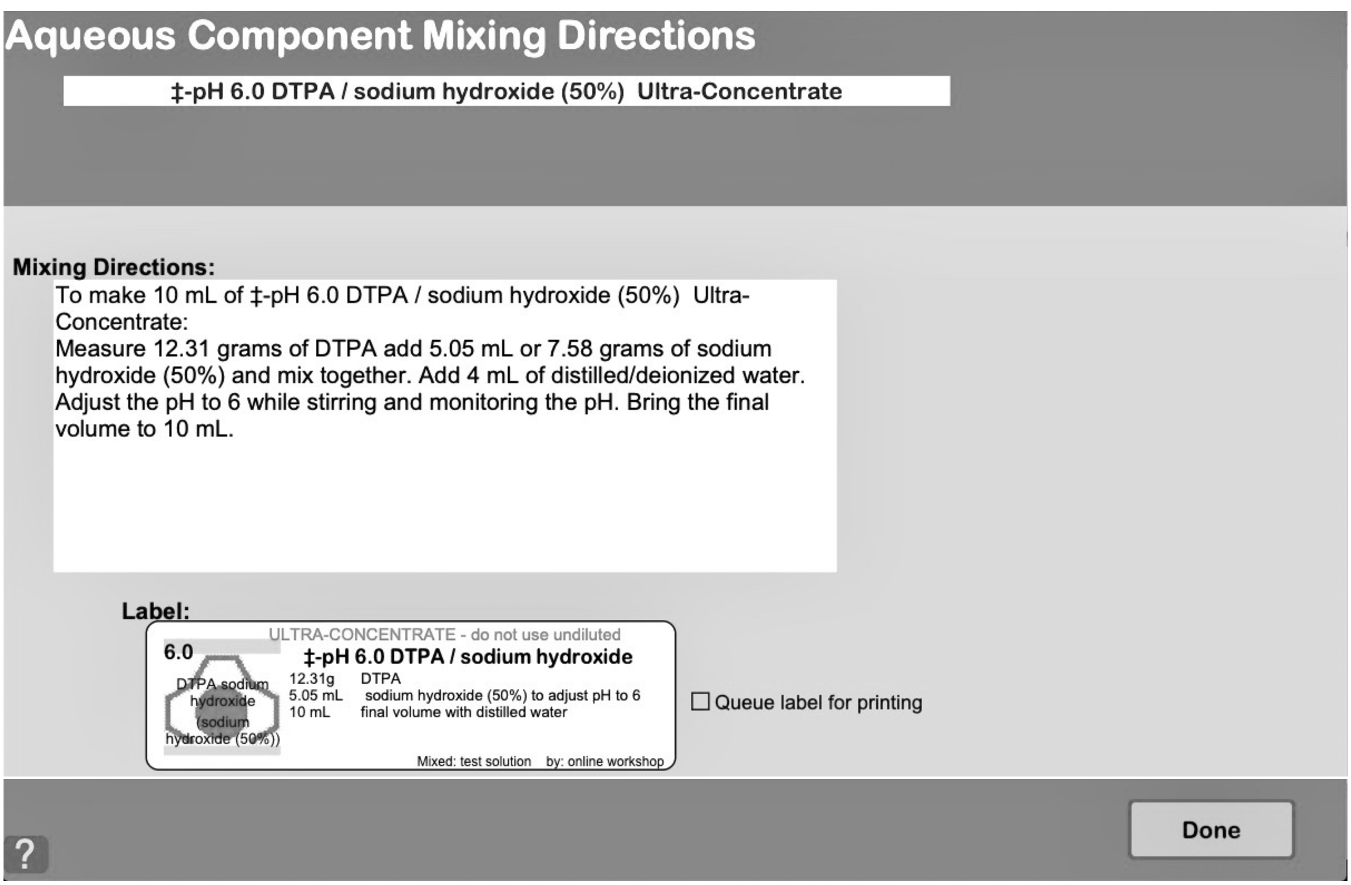
Note: Ultra-Concentrate stock solutions are only used for pH buffers and chelators. (Adding an additional surfactant to a stable microemulsion would be the surest way to break the emulsion.)





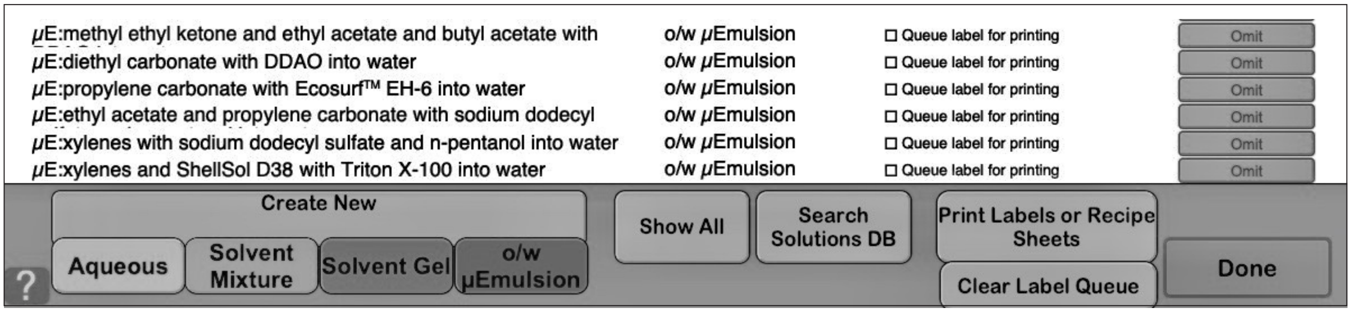
Above is the specification page for the Ultra-Concentrate pH 6.5 DTPA solution. You will notice it's made with 50% sodium hydroxide solution rather than the normal 10% solution.

Below is the recipe page which shows the computer-written recipe as well as the label. I still have to design a new label style for the smaller vials which will hold the Ultra-Concentrates.

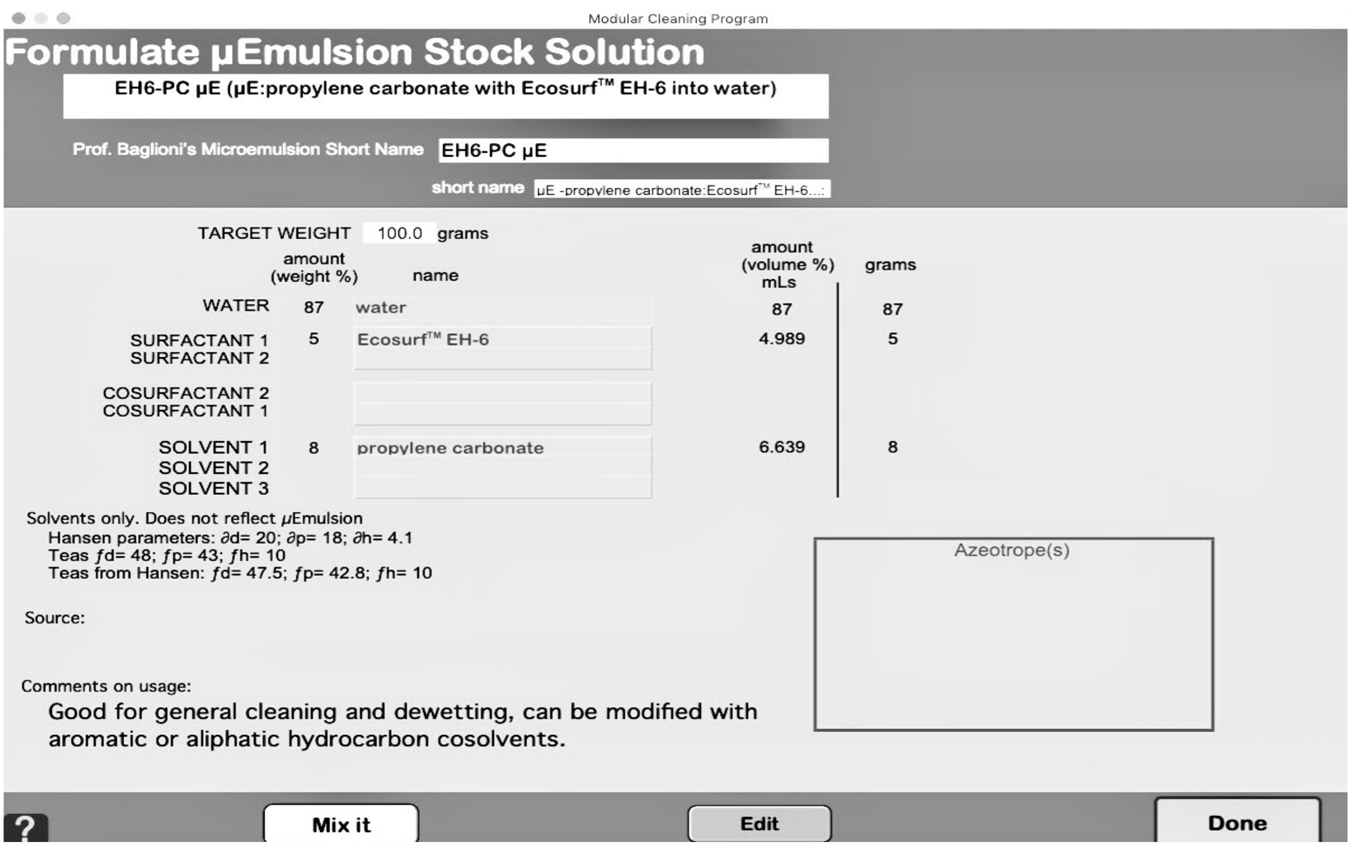


Microemulsion Stock Solutions

Now that we know we can adjust pH and add chelator Ultra-Concentrates to stock microemulsion solutions, it's time to examine the stock microemulsion solutions themselves, designated with "μE:" at the beginning of their names in the solutions database (μ = micro, pronounced "mew," E = well, you get it).



And here is what the specification page for a microemulsion looks like:



As is the case with solvent gels, the MCP can't predict what combination of surfactant(s), cosurfactant(s), solvent(s), and water will make a functional microemulsion. However, with a known recipe, we can specify that microemulsion in the MCP. That microemulsion can have up to two surfactants, two cosurfactants, and three solvents.

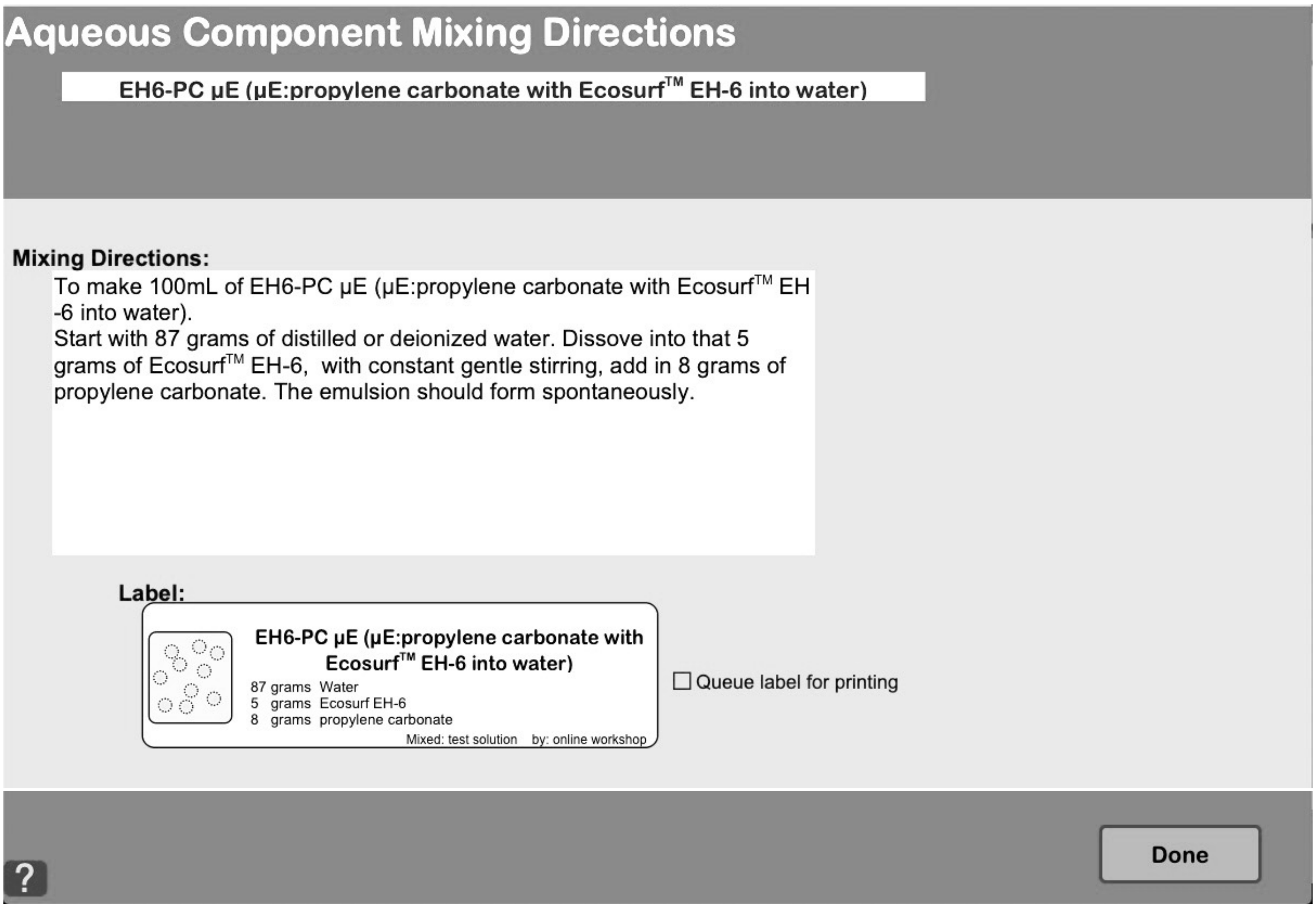
The MCP solution name is generated by combining "μE:" with the names of the solvent(s) first, then the surfactant(s), followed by the cosurfactant(s), and finally "into water."

I've also added Dr. Baglioni's Microemulsion naming convention which is shorter but not quite as complete. It lists the surfactant first, a dash and abbreviations for the solvent followed by μE.

In the above example, the MCP name is "μE:ethyl acetate and propylene carbonate with sodium dodecyl sulfate and n-pentanol into water" which is completely descriptive but way more than unwieldy. Under Baglioni's naming system, the microemulsion is known simply as EH6-PC μE.

There is also space for a general comment on what each particular microemulsion works best to dewet or solubilize. And while they are of no particular value, potential azeotropes and solubility parameters for the solvent(s) and cosurfactant(s) are tabulated. All bets are off once the solvent mixture goes into the micelle forming the emulsion.

Remember, too, that microemulsions are formulated by weight percent. On the left side of specification page are the weight percent values while the two columns to the right give the volume and weight of each component to build the target weight of microemulsion desired. Clicking on “Mix It”, as always, takes you to the recipe page.



In Practice

After preparing the microemulsion stock solutions and the Ultra-Concentrate pH buffers and chelators, we have a panoply of cleaning options. As with the conventional MCP, we can quickly mix test solutions. Starting with 5mL of one of the stock microemulsion solutions we can add the appropriate amount of the Ultra-Concentrates, in this case a pH 5.5 buffer. You can see on the page below that to adjust the pH of the microemulsion, above, to pH 5.5, we would add 0.06 grams, 1 drop, or 39μL of the pH 5.5 Ultra-Concentrate solution.

Add a chelator to the mix? As with the traditional MCP, we build a new solution for a new test in a new small cup. To make a test solution with both a buffer and a chelator, starting with 5 grams of the microemulsion stock solution to which is added 0.06 grams of the pH 5.5 Ultra-Concentrate pH buffer at pH 5.5, and 0.06 grams, 1 drop, or 59μL of the pH 5.5 citric acid Ultra-Concentrate chelator solution.

Why are both solutions at 0.06 grams? Both solutions are concentrated 62.5x so by weight the amount is the same.

Why are the amounts of each Ultra-Concentrate solution lower than expected? You will note that in the top left corner, the program lets us know that we are using a microemulsion that contains 73% water, so the amount of Ultra-Concentrate (2 drops, 80μL, per 5mL water) is reduced proportionally.

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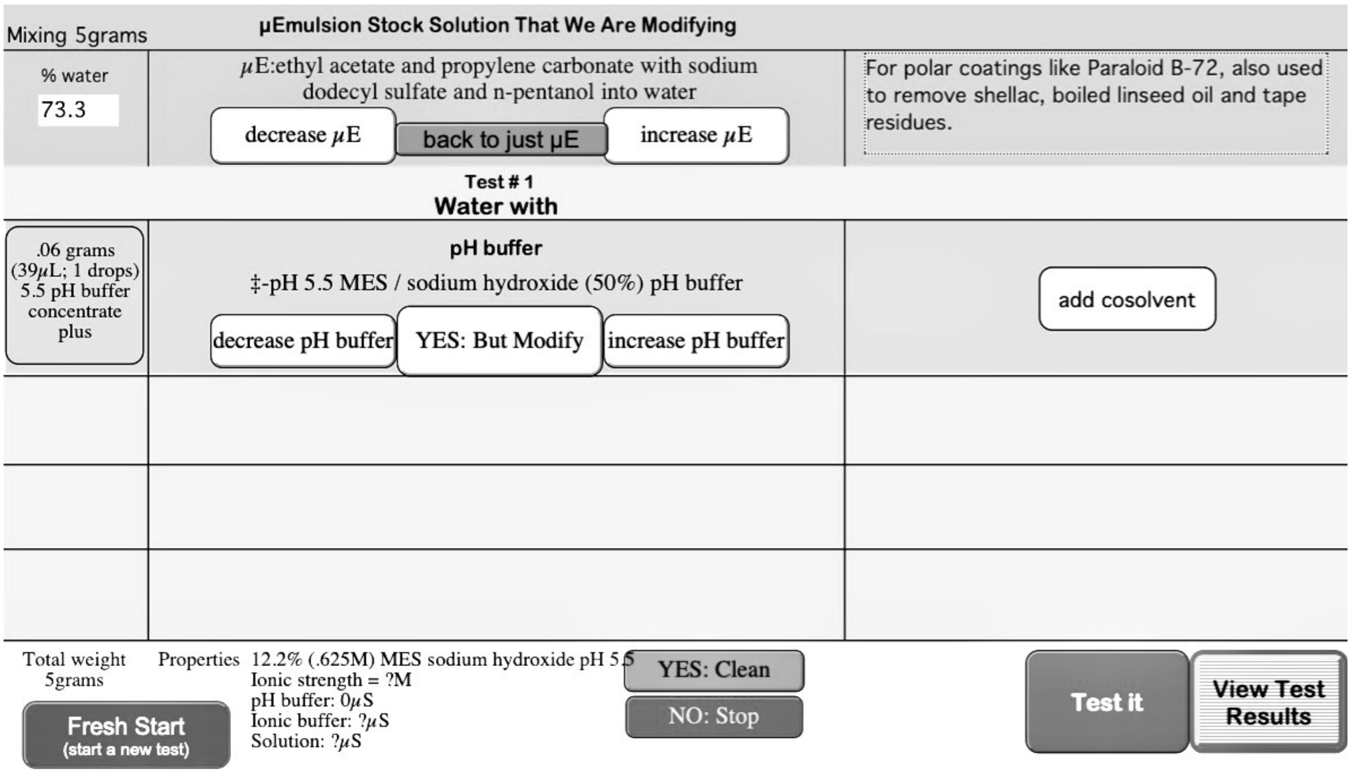

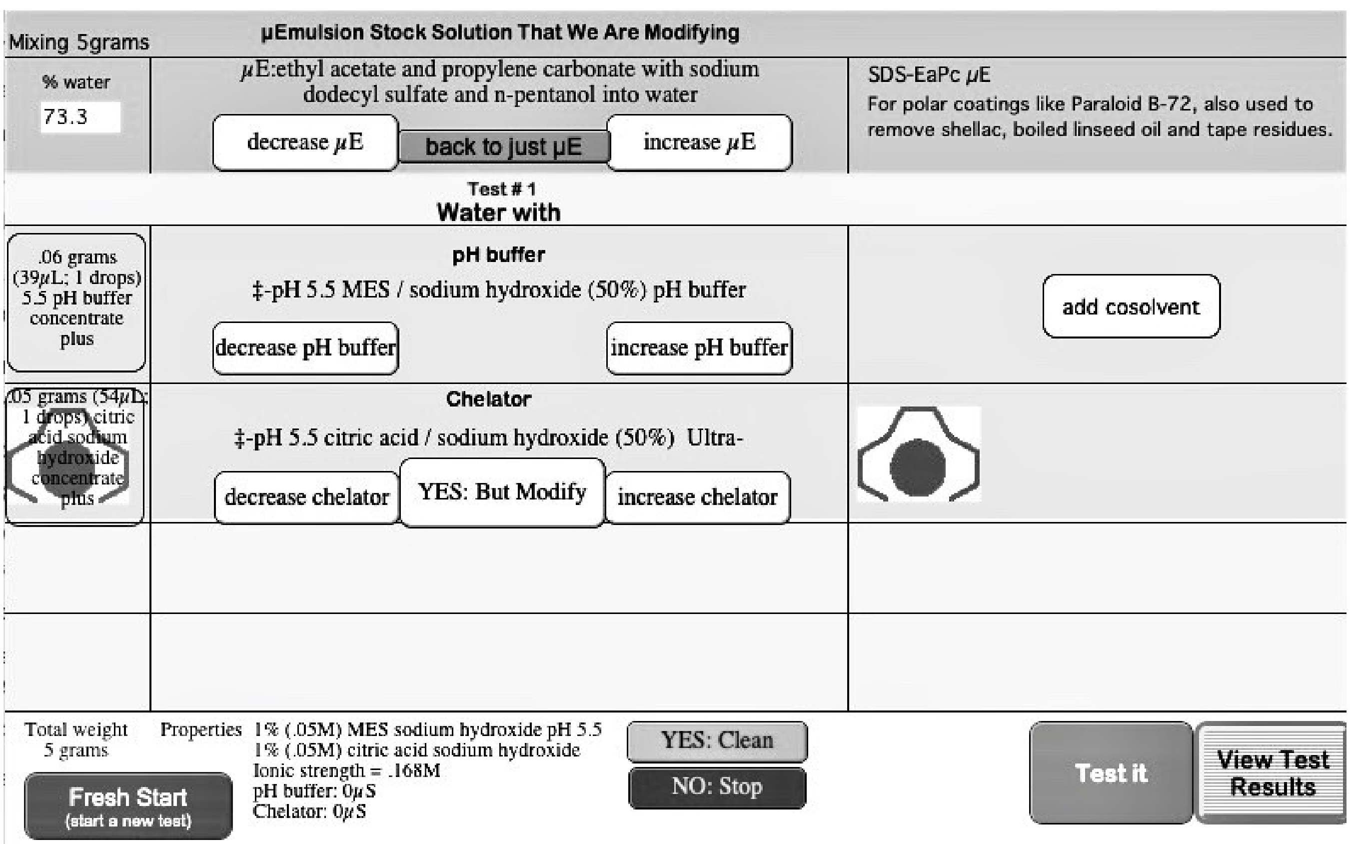

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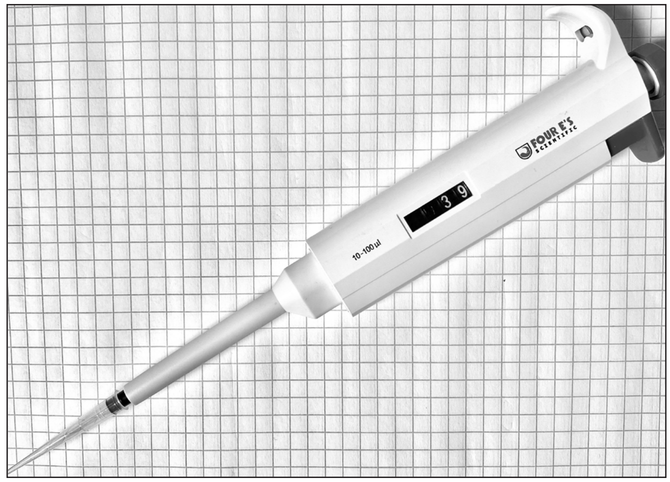


Why is the buffer Ultra-Concentrate 39μL while the citrate is 59μL? Remember that microemulsions are built by weight percent. Since the densities of each solution are different, the conversion from grams to μL gives different volume values.

So, why does each list 1 drop of Ultra-Concentrate solution when the volume listed in μL is different? The volume resolution of a conventional dropper is by whole drops.

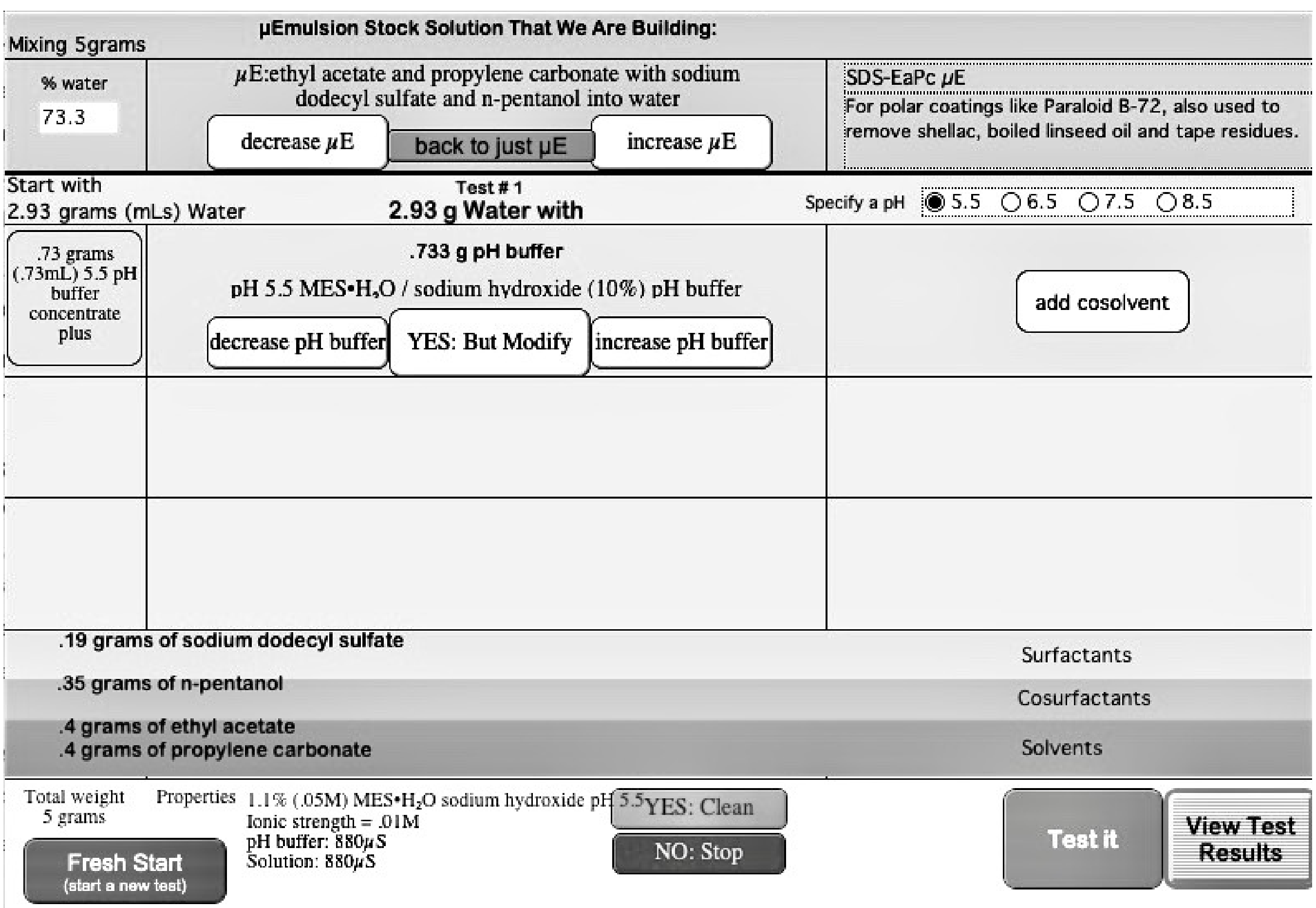
(Ever try to measure ¼ drop?)

So, to be more accurate in the mixing of the test cleaning solutions, I hereby add a micropipette to the list of MCP supplies. (A 10-100μL micropipette can be purchased on Amazon for \$30 plus 1,000 200μL pipette tips for an additional \$9.)

The Same Again, But Different

If you have a traditional MCP solution set with the 5x concentrates rather than the 62.5x Ultra-Concentrates, are you out of luck? Of course not!

In this case we build a new microemulsion in 5mL test solutions for each test. This time we use a solution set built with the same stock microemulsions but with the traditional 5x concentrate stock solutions. Here's how to build the pH 5.5 buffered SDS-EAPC μE illustrated below:



To make 5mL of the microemulsion, start with 2.93 grams of distilled/deionized water and add 0.73 grams of stock pH 5.5 buffer solution concentrate. To that 3.66 aqueous solution, add 0.19 grams of sodium dodecyl sulfate (SDS) and dissolve it in the aqueous solution; add, dropwise with gentle stirring, the 0.35 grams of n-pentanol, 0.4 grams of ethyl acetate and 0.4 grams of propylene carbonate.

Nostalgia

And, of course, we can use the new Ultra-Concentrate solutions to build conventional MCP aqueous solutions.

We use a solution set built with Ultra-Concentrate pH buffers and chelators and the conventional 5x surfactant concentrates and the gel stock solutions (as well as ionic strength modifiers for the complex cleaning system).

We use 2 drops (80μL) of the Ultra-Concentrate and 1 mL of distilled/deionized water to replace the conventional 1mL of 5x stock solution. It's 1+1+1+1+1=5 with a couple of extra drops of Ultra-Concentrate.

Below is the standard pH buffer alone.

And, at right is a complete gelled solution with 5.5 pH buffer, citrate chelator, Ecosurf EH-6 surfactant, gelled with Xanthan gum.

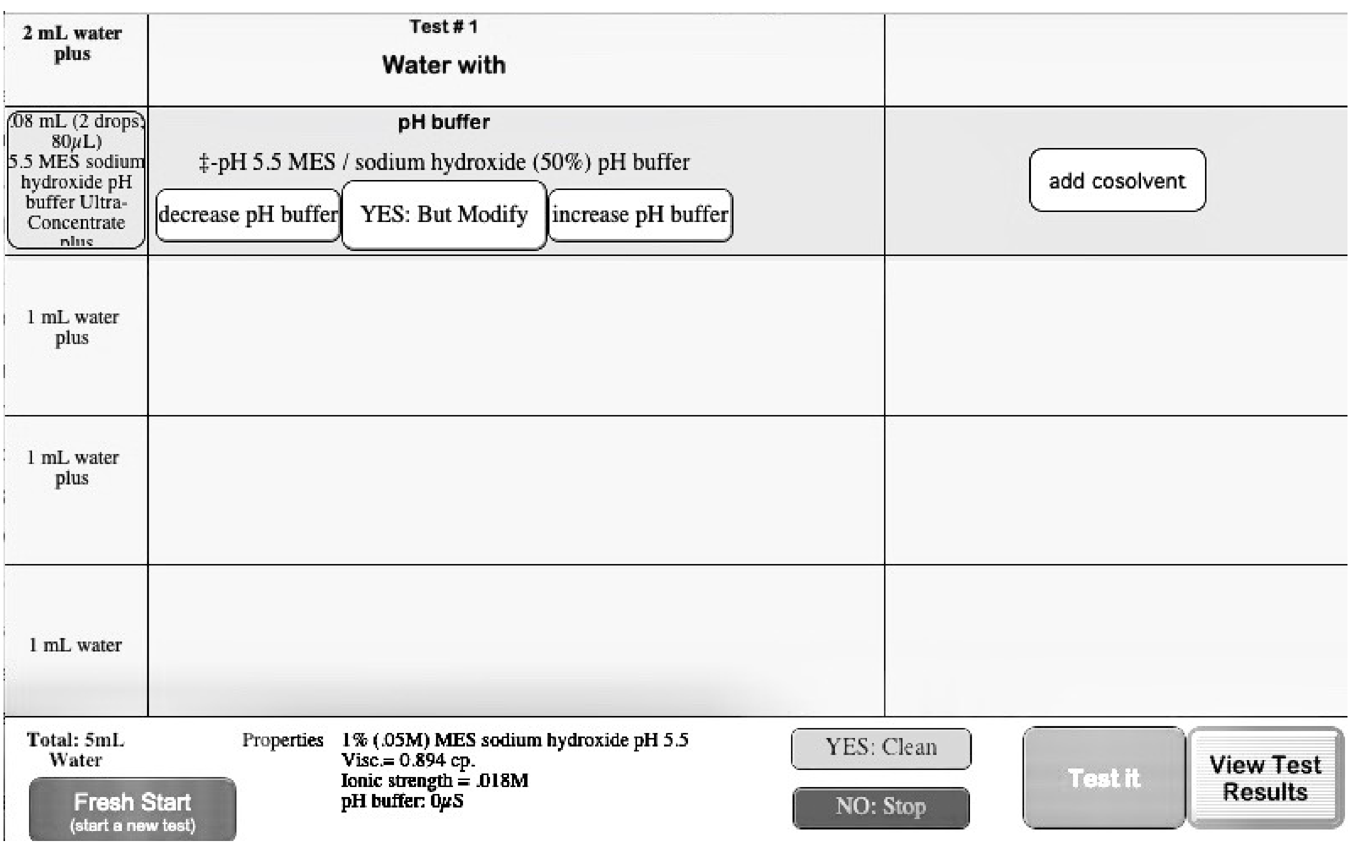
Start with 3mL distilled/deionized water; add 2 drops (80μL) pH 5.5 Ultra-Concentrate buffer solution; 2 drops (80μL) pH 5.5 citrate Ultra-Concentrate chelator solution; 1mL of the Ecosurf EH-6 surfactant concentrate (5x concentrate) and 1 gram of the Xanthan gum gel concentrate.

(A tip: Using a battery powered milk-frother to mix the gel into a smooth solution is a great trick. However, if a surfactant is present, the gel foams while mixing. Unless you want a fluffy mousse, it is better to wait until the gel has formed and then stir in the 1mL of surfactant concentrate.)

So Where Are We Now?

Just like your favorite computer program, each upgrade makes things more complicated. I like to think the added complication to the MCP will not be as traumatizing as the last version change to Photoshop proved to be. And, I'm still trying to get used to the new auto-correct feature in Word.

So, if you're not ready for microemulsions, the program offers all the same, familiar options. Just ignore the "emulsions" button. If you want to try playing with the new Baglioni-style microemulsions, look through your chemical storage and find what materials you have and what you need to buy. Make just one of the stock microemulsions. Try it out – have some fun.



If you want to go all out, look through the recipes paying attention to the “comments on usage” notes. Pick a few microemulsions that cover the materials you deal with in your studio.

When using a microemulsion to dewet a coating, you want to expose the surface of the coating to the microemulsion for some time – anything from 15 seconds to hours. You want to keep that surface consistently wet. You can use tissue or Evolon to maintain contact of the solution with the surface of the coating. Placing a piece of plastic wrap or Mylar on top of that can keep the tissue from drying out too quickly.

You can also infuse any of the CSGI gels by soaking them overnight in the microemulsion. The CSGI line of “Dry” gels hold aqueous materials most strongly so they can be used on water sensitive surfaces. They are crystal clear but are not very flexible.

The Peggy gels are much more flexible but are not transparent and not as water retentive. You can cast agarose gel into 2mm thick sheets or desired shapes and soak that overnight in a microemulsion solution. Luke is recommending the use of Agarose SS (Super Strength) as it forms a more cohesive film than normal Agarose.