



Choosing Thickening Agents For Emulsions, Part I: Water Phase Thickeners



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As readers of this column certainly must by now know, emulsion stabilization is a favorite topic of mine. A key component of every emulsion is the thickener or, more properly, a thickener system that is employed. We all remember the Stokes Law, which tells us that an important factor in stabilizing emulsions is the viscosity of the external phase. Interestingly enough, often the primary function of thickeners is not to increase the viscosity of the emulsion, but to stabilize the emulsion or to affect application qualities.

The choice of thickeners is almost limitless, with more being developed practically every day. This short column will discuss a few thickeners and things to keep in mind when choosing them. It is by no means comprehensive, and I'm fairly certain that I won't be discussing your favorite material.

There are a number of factors to be considered when choosing a thickening agent for emulsions, but the most important one is to remember your goal. To say it another way: Why are you using a thickener? Is it to increase the viscosity, stabilize the emulsion, effect application qualities, or suspend some particulate material?

In regards to increasing the viscosity, we know that this can be accomplished in two ways: increasing the volume/size/percentage of the internal phase, or increasing the viscosity of the external phase (see previously mentioned Stokes Law).

Application Qualities

Few things are more important than an emulsion's application qualities. When discussing this parameter, there are some important elements to take into account.

Playtime: How long does it take for the emulsion to rub in? This can be (and usually is) dramatically affected by the inclusion of a gum/thickener. It is also affected by the type and concentration of the emollients in the internal and external phases. If you have, for example, a liquid makeup that contains high levels of particulates, you must have sufficient playtime to allow the product to be applied and cover the skin while also having a quick drying time. Otherwise, the liquid makeup will be considered oily. On the other hand, a sunscreen must not dry too quickly or it cannot be spread evenly to provide complete/uniform protection.

Cushion: "Cushion" is a difficult concept to put into words because it is a perceived quality, so it is quite subjective. Generally, cushion refers to the apparent thickness during the rubout of the emulsion. If the cushion is too little, then the emulsion will feel thin and not luxurious. Cushion can be affected by a thickener, the humectant used (for example, butylene glycol and hexylene glycol have less cushion than glycerin or propylene glycol) and the "oil" content and type.

Temperature Stability

Stabilizing the emulsion can be further subdivided: high temperature stability (40°C, 45°C and 50°C), low temperature stability (4°C, -10°C) or freeze/thaw stability. In terms of suspension, the formulator must consider the specific gravity of the material to be suspended along with its surface charge/modification (if any). Additionally, the particulate may change its effect based on pH. Zinc oxide is a good example of this phenomenon - as the pH drops, zinc oxide becomes more soluble, this releases polyvalent "electrolyte" into the system which can have a deleterious effect on the thickening ability of the polymer.

When talking about stability and viscosity, a formulator should always measure the viscosity of the emulsion at room temperature and at high temperature as a predictor of emulsion stability. If, for example, the viscosity of the lotion is 10,000 cps at 20°C but drops to 100 cps at 45°C, then you should be concerned. If the viscosity only reduces to 5,000 cps at 45°C then the formulator can have a real measure of confidence of the long-term stability of the lotion.

Gums and Thickeners

Emulsion stabilization can also be accomplished through the use of hydrophobically modified gums. There are many

such materials currently marketed, and I urge you to investigate these versatile materials. But, beware of using hydrophobically modified gums in formulations with high levels of emulsifiers – destabilization may result due to flocculation depletion (a competition at the interface between the emulsifier and the hydrophobically modified gum). There are specific things that govern which thickener to use and at what percentage.

pH: Many gums and thickeners will profoundly change their efficiency based on the pH of the system. For example, if you are formulating an AHA lotion with a pH of 3.5 and incorporating lactic acid at 5%, the use of carbomers is not a good idea because they are acrylic acid polymers and must be neutralized to a pH of at least 5.5 to exhibit functionality. You might consider a cellulose derivative combined with xanthan gum or magnesium aluminum silicate. Polyacrylamide or hydroxyethyl acrylate/sodium

acryloyldimethyl taurate copolymer would also be a good choice, as these materials have good thickening characteristics at low pH. If a hair relaxer was formulated with a pH above 12 and a very high electrolyte load, acrylates/stearate-20 methacrylate copolymer might be used because it tolerates these conditions well.

Electrolyte: There are two things to consider when discussing electrolytes: type and concentration.

Is the electrolyte type monovalent (sodium or potassium) or polyvalent (calcium, magnesium, zinc, aluminum, etc.)? Some gums are more tolerant to electrolytes and specifically to the polyvalent type. Sometimes the neutralizer (when the polymeric thickener must be neutralized) can dramatically improve the electrolyte tolerance. You should also remember that neutralization can play a major role in the final stability of the formulation. Generally, the material should be neutralized before it “sees” the electrolyte.

Generally the “natural” thickeners have better electrolyte tolerance than the synthetic materials. However, as a general rule, the natural materials are not as good/efficient in building viscosity or stabilizing emulsions.

Viscosity desired: I would not recommend using gums/thickeners for significantly increasing viscosity of emulsions. In order to accomplish this, they must be used at levels that degrade the skin-feel qualities of the emulsion.

Ionic nature of the emulsifier: If the emulsifier system is nonionic, you can readily employ any thickener. However, if you are making a skin cream based on cationic emulsifiers (baby or dry skin lotions, for instance), you should consider using a cationic thickener such as polyquaternium-37 or polyquaternium-32.

Cost: This is always an important consideration. In general, the thickeners we are discussing are used at a sufficiently low level, so cost contribution is not an issue. However, some exotic natural (sclerotium gum) and synthetic (acrylic acid/acrylonitril copolymer) gums, which offer excellent skin feel and stabilization, can be quite expensive. They can often be utilized in combination with other materials at low use levels while still applying their significant benefits.

Skin feel: This cannot be ignored! The natural materials generally provide great lubricity but, if used at concentrations that are too high, they can get sticky and negatively affect playtime. Using particulates (nylon, hydrophobically modified starches, PTFE, polymethylmethacrylate, etc.) can dramatically improve skin feel.

Stability/compatibility with key materials: If you have developed an emulsion that contains reactive materials such as hydrogen peroxide, hydroquinone or dihydroxyacetone, then you must determine the compatibility of your chosen gum with these materials.

Application characteristics: The rheology of the emulsion is very important. A cream should shear thin during application and then thicken up (thixotropy) after rubbing to

give a rich skinfeel. This can be controlled/influenced by your choice of gum/thickener.

Marketing claims/issues: With the move toward “natural” cosmetics (which has been going on for several decades), we’re seeing the use of natural thickeners expanding. I suggest combining them with newer synthetic thickeners in order to get real synergism and performance.

The thickener category changed dramatically several decades ago with the introduction of the carbomer materials by the B.F. Goodrich (now Noveon) Company. These synthetic polymers can be loosely described as a homopolymer of acrylic acid that has been crosslinked. As supplied, this off-white powder is in its acid form. When neutralized with an appropriate base (triethanolamine, sodium hydroxide, potassium hydroxide, etc.), the acrylic acid groups become acrylate anions (negatively charged) and repel each other. This repulsion opens up the polymeric backbone, and thickening is the result.

Since the carbomers depend on electrostatic repulsion to thicken, it is not surprising that they exhibit a poor tolerance to high electrolyte (sodium chloride) levels. They are even less forgiving of polyvalent electrolytes (zinc oxide, calcium chloride, magnesium sulfate, etc.). Thus, if you are formulating a sunscreen containing zinc oxide and need to use a good suspending agent, these materials are to be avoided. In this case, you might consider using a more robust polymer such as acrylates/acrylamide copolymer or polyacrylamide.

Many people have had success using a natural thickener such as xanthan gum in combination with a mineral thickener (magnesium aluminum silicate). The carbomers became popular for a number of reasons, but they had three major benefits when compared to other thickeners of the time: they increased viscosity at low concentrations, they were excellent suspending agents, and they maintained most of their viscosity at high temperatures. There are now numerous materials available that have similar (and sometimes better) performance, but carbomers is where it started.

Let me end with one of my favorite rants - we don’t combine thickening agents often enough. It is more typical for us to use a single material and, if it doesn’t seem to work, we just increase its usage level until price or skin feel considerations force us to abandon it for another material. Remember that it is difficult to sell an emulsion that feels like wallpaper paste! Combine thickeners . . . save money, improve skin feel and improve stability.

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