RHEOLOGY OF EMULSIONS DOCUMENTARY

Effects of processing on the rheological behavior of emulsions

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Mixing

Mixing is basic to the compounding and processing of emulsions in the cosmetic industry, but its potential effect on the rheology of a product is often overlooked. Mixing is necessary to blend a water phase and oil phase into an emulsion, but consider the potential effect of the degree of mixing on the product viscosity. First of all, a minimum amount of energy must be developed to evenly mix the two phases and subsequent additives. A high amount of mixing energy, however, has the potential of decreasing the particle size of the dispersed phase and hence affecting the emulsion viscosity. The timing of this mixing energy can also be important, as the product is finished off and cooled to filling temperature. In the case of a lotion, which is usually cooled to room temperature, viscosity can increase tremendously as the product is cooled. If the mixing energy is kept constant during the cooling cycle, it begins to have more of an effect as the viscosity increases. This means that a short period of mixing at 90°F can have a greater effect on viscosity than a long period at 150°F. If the product is shear-thinning (pseudoplastic or thixotropic), the viscosity will decrease. In many cases, this viscosity reduction is not completely reversible.

During the process development stage of a new product development program, close attention should be paid to the interrelationships between mixing and product rheology. Bench formulations are usually done in small beakers (4-5″ in diameter) with laboratory Lightnin' mixers[a] with perhaps a 2″ diameter propeller moving at 1800-3600 rpm. This represents a prop to tank diameter ratio of about 0.4. In the plant, however, this ratio is more likely to be about 0.2. The turbulent mixing achieved on the bench can therefore become a gentle blending (almost laminar flow) in scaleup, which can dramatically affect the product's rheology and even make it nearly impossible to dissolve some difficult ingredients. Of course, mixers and their motors can be designed and built to handle almost any requirement, but they then become special order items which are very expensive and carry long lead times. The power requirements of a mixer are related to impeller speed and diameter and product density and viscosity.[3] For thin product, power $\alpha\ N^3D^5$ where N is the impeller rpm and D is the impeller diameter. For heavy, viscous products, power $\alpha\ N^2D^3$. One can see from either relationship that the impeller diameter has more effect on power requirements than impeller speed, and yet the impeller to tank diameter ratio has a large bearing on the degree of mixing that will occur in a batch tank.

Assuming some foreknowledge of the type and degree of mixing required in processing an emulsion, a wide variety of mixers can be employed. Instead of the well-known propeller, a mixer can have rakes, gates, spirals, paddles, axial flow turbines, radial flow turbines, or contrarotating blades. When scaling up a process with an emulsion that is heavily dependent upon mixing, one should investigate not only different types of impellers but also different impeller to tank diameter ratios.[4] This optimization can lead to a more economical process, substantial capital savings, and sometimes even an improvement in the product properties. At the very least, however, plant mixing conditions should be duplicated as closely as possible if the product is planned for production in existing equipment. This is a common source of scaleup problems. Not only can the mixer affect the product viscosity, but the product viscosity can

[a] Mixing Equipment Co., Inc., Rochester, NY.

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also affect the degree of mixing. If a propeller is utilized to mix a viscous product that is shear-thinning, it will cut a hole in the center and leave the bulk of the product unmixed. If a product happens to be shear-thickening, it could gradually build up in viscosity to the point where the mixer motor is overloaded.

The type of mixing required also has a bearing on mixer selection. For dispersion and emulsification applications, a high level of shear is usually required. This can be achieved by a small impeller run at high speed. For blending and heat transfer, a high level of flow is desirable. This can be achieved with a large impeller running at a low speed. In the case of heat transfer, viscous lotions are usually handled with a contrarotating agitator with side-scraping blades. The blades are needed to remove the cold, more viscous product (or solids baked on during heating) from the heat exchange surfaces to maintain heat transfer efficiency. Sometimes two different types of mixers (high shear and high flow) are used in the same tank to perform mixing at different stages in the product manufacture. Where this is not feasible, the mixer is chosen on the basis of the most critical mixing step. For example, if heat transfer and blending during the viscous stage of the product cycle are the most important, then contrarotating side scraped agitation (low shear, high flow) will be used for emulsion formation as well as during the cool down stage. If high shear is as critically important as side scraped contrarotating agitation, the two can be accomplished in equipment such as the Eppenbach Agi-Mixer,[b] which combines the high shear of an Eppenbach Homo-Mixer, centrally mounted, with a side scraped contrarotating agitator. On the bench, contrarotating agitation can sometimes be approximated with a Planetary Mixer.[c]

Mixing is so basic to the formation of emulsions and can have such an important effect on product rheology that the smart formulator will learn to work with it in achieving the desired end properties instead of fighting against it in a dogmatic scaleup from benchtop to plant. Cosmetic emulsions may be shear sensitive to some degree, and mixing can be used as a tool in achieving the desired product viscosity by properly manipulating the mixing variables.

Heating and cooling

The variables involved in heat transfer operations are the mass or volume of product and its specific heat; the temperature differential of the heating/cooling medium and the product; the heat exchange surface efficiency; and the relative flowrates of the heating/cooling medium and the product. Practically speaking, however, several of these variables are summed up in the process parameters of heating/cooling rate and the work input (mixing) during the heat transfer stages.

Heating is generally less of a problem in cosmetic processing because the product or phase is usually fluid at elevated temperatures (viscosity being inversely proportional to temperature for emulsions commonly encountered in the cosmetic industry). It can be a problem when heating a viscous product from room temperature because the product may tend to bake on the heat exchange surface. This is where side scraped, contrarotating, or single sweep agitation is effective. If the material is shear-thinning, then high shear agitation is usually effective if it is not permanently detrimental to ultimate product viscosity. Cosmetic emulsions such as water-in-oil creams are usually filled while hot in order to reduce the viscosity to aid filling. The rate of heating is not usually considered an important parameter, assuming that the desired end point is not overshot. Work input is also of minor importance because less energy is imparted to the product when it is in the fluid state, and because the material is amorphous at this stage.

Cooling is more commonly a problem with cosmetic emulsions because it generally increases product viscosity greatly. A side scraped agitator is essential when cooling an emulsion below its solidification point, or the product will form a heat exchange barrier on the exchange surfaces and drastically reduce efficiency of heat transfer. In addition, as the product thickens the mass and heat transfer rates decrease. This also slows the rate of cooling. When temperature is plotted against time, the curve is usually a decreasing exponential. The only way around this is to minimize the product mass to be cooled, maximize the heat exchange surface, and still provide for the heat exchange surface to be scraped. This is accomplished in the industry with a Votator[d] which is a scraped surface, continuous heat exchanger. The Thermutator[e] is a similar unit. The efficiency of this type of equipment is high because of its high ratio of cooling capacity to product flowrate. This is illustrated by the much higher heat exchange coefficients (in Btu/hr—ft^2-°F) obtained in a Votator as opposed to a stirred tank.

	Heating	Cooling
Stirred tank	150	80
Votator	500	250

The effect of cooling on product rheology can best be illustrated by comparing the continuous cooling of a Votator with the batch cooling in a kettle with a side scraped contrarotating agitator. The rate of cooling of the Votator is much faster than that of the batch; the batch tends to form a smaller crystallite (particle) size as the solid ingredients solidify. The distribution of these crystallites also tends to be very narrow. In con-

[b] Gifford-Wood Co., Hudson, NY.

[c] Hobart Corp., Troy, OH; or Charles Ross & Sons, Hauppauge, Long Island, NY.

[d] Votator Div., Chemetron Corp., Louisville, LA.

[e] Cherry-Burrell Div., AMCA International, Cedar Rapids, IA.

trast, the batch cooling tends to form larger crystallites over a much wider distribution range. The effect this has on product rheology differs from formulation to formulation, but sometimes the emulsion treated to quick cooling in the Votator will be thicker than its batch-cooled counterpart (neglecting work input) because the crystallite size is smaller and more evenly dispersed. Its uniformity and sometimes even stability is also usually superior because of the more narrow crystallite distribution.[6] Although it is theoretically possible to vary cooling rate in a batch tank to achieve a particular crystallite growth rate, the rate is usually fixed by nonthrottling cooling medium valves and pumping limitations. Switching from tower water to chilled water, however, could have a step effect on crystallite growth.

The effect of differences in mixing energy (work input) is harder to define for the two processes, but this parameter is important when attempting to achieve a final product viscosity. It is generally found that work content, if it has any effect at all, is inversely proportional to the emulsion viscosity. The more work put into an emulsion during cooling the lower the viscosity usually is. This is because most cosmetic emulsions in creams and lotions have thickening systems that are shear-thinning and not perfectly elastic. That is, when sheared beyond a minimum amount they will not rebuild to the original viscosity. In this respect, the Votator usually puts more energy into an emulsion during cooling than the batch process and hence can have more of a reducing effect on product viscosity. The rotating scraper blades of the Votator can be driven up to about 600 rpm and work on a relatively small volume of product, so even though the product is exposed for only a short period of time, it is subjected to high energy input.

Conversely, the mixing blades of a side scraped contrarotating agitator rotate at relatively low speeds (less than 30 rpm, although the tip velocity can be quite high for a large diameter agitator) and work on a large volume of product. The average work input is therefore low, but if left going for a long period of time (especially at the lower temperatures) the total level of shear produced by such an agitator can equal or even exceed that produced by the Votator. Mixing times are usually kept to a minimum in a batch process, however, in order to keep batch cycle times to a minimum.

In summary, an emulsion is usually heated after it has been formed to reduce its viscosity for filling. Cooling has a more important relationship to final product viscosity because of its effect on crystallite size and dispersion, and because of the interrelationship of work input and product viscosity. Scaleup problems are sometimes encountered because the cooling rates and/or energy input achieved during bench formulation cannot be duplicated in production equipment. This is an area in which process development can make significant contributions towards a successful startup.

Shearing

The effect of shear on product viscosity caused by propeller mixers, contrarotating agitators, and the Votator have already been touched upon. These are generally considered to be low energy input devices. Other equipment which produces a shearing action of a low energy nature are transfer pumps, piping, filters, filling machines, and the like. Although non-Newtonian fluids can be either shear-thickening or shear-thinning, many emulsions encountered in the cosmetic industry are shear-thinning. This discussion will therefore assume that emulsion viscosity decreases with increasing shear, although the effect of the processing will simply act in reverse for shear-thickening fluids.

The main emphasis in scaling up a new product is usually on the compounding portion of its production. Subsequent handling, however, can sometimes cause permanent viscosity reduction to nonelastic systems from shearing. In a typical operation, a finished emulsion is cooled to room temperature in a compounding vessel, and then pumped through a filter to a storage tank where it is held for filling. The pump itself creates some shearing energy as it pushes the product. The walls and configuration of the transfer piping produce back-pressure (usually expressed as a function of pipe lengths) and increase the shearing stress on the product. A strainer in the line which is used to trap large particles and debris also produces backpressure and shearing stress. If the product is particularly inelastic in recovering from shear stress, viscosity will have been reduced by this transfer step. The product may or may not be mixed in the holding tank prior to filling. If it is, this will impart more shearing stress to the product.

The product may then be pumped to the filling line. This entails another pumping operation which again produces shear stress from both pump and piping. In addition, the restrictions in the filler create more shearing stress. The emulsion may be more vulnerable to permanent viscosity damage due to shearing stress at this point too, because it usually has had a chance to age and build a network of bonds. A portion of these bonds, if broken, are sometimes permanently destroyed. The interrelationship of the pump and filler can be important too. Fillers are constantly cycling on and off. If the filler is pump fed instead of gravity fed and if the pump does not shut off instantaneously with the filler, pressure buildup in the line occurs. Transfer pumps such as the Waukesha DO series[f] come with internal pressure relief valves which recycle the product within the pump until the pump is shut off or the pressure is otherwise relieved. This extra working of the product can have a great effect on the product viscosity because of the

[f] Waukesha Foundry Co., Waukesha, WI.

additional shear stress. External pressure relief loops would have the same effect.

In contrast to equipment that produces a low level of shearing energy, some devices are purposely designed and used to impart high shearing levels to a product. A colloid mill such as the Charlotte Colloid Mill[g] is often used to produce a low viscosity emulsion from one that initially has a high viscosity. The colloid mill is also used to homogenize products in the sense that particles are broken down to a uniform size, but this is sometimes considered secondary in importance to the reducing effect it has on viscosity of shear-thinning systems.

Sometimes high shear is necessary to disperse and dissolve troublesome solids, such as gums and resins, in a liquid phase. In these applications, frequent use is made of such high shear mixers as the Varikinetic High Shear Mixer,[h] the Cowles Dissolver,[i] and the Premier Hi-Vispersator.[j] These mixers depend upon high shear stress developed on sharp edged blades rotating at very high rpm. The Dispersator[j] is a high shear mixer without blades which rotates at high speed while it forces the fluid through slots in its mixer head. This unit has been used successfully to disperse Carbopol in an aqueous system.

In using high shear mixers it is important to realize that the mixing pattern can be important, just as it is for simple mixing. The diameter ratio of tank to mixer impeller and even the vertical placement of the impeller can have a bearing on the mixing pattern and hence the shearing stress. The type of shear created by the Cowles, Varikinetic, and Premier mixers is hydraulic in nature versus the basically mechanical shear created by the colloid mill. The end result, however, can be the same if the product being processed is sensitive to shearing stress.

Homogenizing

Homogenization, or the reduction of particles to a small and uniform size and their even distribution in a medium, is related to shearing in that high shear is frequently used to create the particle breakdown. But homogenization goes beyond shearing in its application. The cosmetic industry usually resorts to homogenization for dispersing solids and insoluble liquids in a liquid phase and reducing the dispersed particles to a minimum size. The reasons for doing this are numerous and include the desire to increase stability by minimizing globule size and hence decrease the chances of coalescence, to reduce particle size of the disperse phase so as to inhibit settling (as per Stokes' Law), and to increase viscosity by forming a finer emulsion.

There is more equipment available for accomplishing homogenization than there are reasons for doing it. Only few representative types of homogenizers will be discussed here. They will be discussed in a roughly ascending order of increasing intensity of homogenization. Some of these devices, although included here under the general classification of homogenizers, are separately described as dissolvers, dispersers, reactors, emulsifiers, and mills and may not be homogenizers in the strict sense of the word. They are included in this section because they are a logical progression up from plain shearing.

The principle of ultrasonics is utilized for homogenization by the Sonolator.[k] This device operates by accelerating a fluid through an orifice. The fluid emerges as a thin, flat stream which then impinges upon a blade. This blade oscillates in a stable vortexing pattern and sets up ultrasonic vibrations which create particle size reduction. The Sonolator has been used for homogenizing cosmetic creams as well as tomato sauce. The Oakes Continuous Automatic Mixer[l] consists of a shear head with a circular rotor and stator that have intermeshing rows of pins. As the rotor moves at high speed it breaks down and disperses one phase in the other. It has been used for injecting air of a uniform bubble size into an emulsion at a controlled rate, although it is claimed to be useful for liquid/liquid and liquid/solid as well as liquid/gas systems.

The Eppenbach Homo-Mixer, sometimes known as an Eppenbach Colloid Mill,[b] depends upon high velocity fluid flow through a flow restriction to create the shearing stress necessary for homogenization. The blades at the bottom of the unit (immersed in the fluid) rotate at high speed and pump the crude dispersion through a stator which contains restricted openings. The shear caused by the turbine-stator arrangement breaks large particles down to smaller ones. It does have the disadvantage of being a batch-processing device, which means that not all of the batch will pass through except after a significant number of turnovers (and a statistically small percentage will never be processed). It has proven effective in dispersing Bentone clay powder in a wax phase and similar applications, where swelling of the thickener is dependent upon an optimum particle size distribution.

The previously discussed Charlotte Colloid Mill also serves where homogenization is specifically desired for particle size reduction. It produces this reduction by the mechanical action of a grooved rotor shearing the product against a stator while the fluid is being forced through a specific gap clearance (typically, .003″ to .020″). This device has been used to good advantage in dispersing zinc oxide powder in a glycerin medium, where particle size distribution is important in minimizing settling of the solids. A different kind of homogenization is achieved by the three roll mill[c] which creates a grinding as well as a shearing action on the product to obtain a particle size reduction. This

[g] Chemicolloid Labs, Inc., Garden City Park, NJ.
[h] Gaulin Corp., Everett, MA.
[i] Morehouse-Cowles Inc., Los Angeles, CA.
[j] Premier Mill Corp., New York, NY.

[k] Sonic Corp., Stratford, CT.
[l] E. T. Oakes Corp., Islip, Long Island, NY.

mill is typically used to produce dispersion of pigments in a liquid carrier, such as lip pastes for lipstick manufacture.

A high pressure pump can be used for high intensity homogenization, such as the Gaulin Homogenizer and Gaulin Sub Micron Disperser[h] or the Cherry-Burrell Superhomo Homogenizer.[e] These units operate on the principle of hydraulic shear and intense turbulence caused by product being put under very high pressure (up to 8,000 psi continuous service, higher on an intermittent basis) and directed through a restricting orifice to an area of much lower pressure. At this point, energy which has been stored as pressure is instantaneously released as a high velocity stream and the product impinges with shattering force and change of direction on an impact ring. This variety of homogenization is very intense and very effective in obtaining dispersion with a very fine particle size. These homogenizers can be obtained with single- or two-stage homogenizing valves, in different pressure and flowrate capacities, and even with pressurized feed pots and explosion proof motors. Gaulin homogenizers have been used in a wide variety of applications such as cosmetic lotions, lacquers, nail polish, and tomato sauce. This type of homogenizer is useful mostly for low viscosity fluids (under 500 cps), however, since it depends upon the generation of high fluid velocities. High viscosity systems which are shear-thinning can be processed since they fluidize under shear stress. Shear-thickening systems can also be processed if they develop their viscosity after the homogenizing valve.

One can see from this very sketchy list that a wide range of homogenization is possible by choosing various types of equipment and operating them within their design parameters. Besides the selection of a homogenizer, however, one must also sometimes consider the processing point at which homogenization is carried out. For example, if homogenization of a w/o emulsion is desired, it very much matters at what point this takes place. If done while the emulsion is hot and both phases still liquid, homogenization will tend to reduce the disperse phase to a minimum size distribution which will impart certain properties (such as increased stability) to the final product when it is cooled down and packaged. If the product is homogenized after some cooling has taken place and viscosity has already started to build, however, the viscosity of the finished product may be permanently reduced. Since either situation could be a valid application of homogenization, the only generalization that one can make is that timing as well as process step must be considered in developing a process to make a product with the desired end properties, and the effects of each on one another must be known.

Summary

Cosmetic processing and manufacture is still somewhat of an art when one considers that no two emulsions seem to behave exactly alike. Forearmed with a basic knowledge of the processing variables discussed above, one can make intelligent guesses on the effects of various processing steps based on similar formulations. The Law of Perverse Probability (also known as Murphy's Law), however, should remind one never to take any anticipated result for granted. The importance of a logical, well-planned investigation into the effect of various processing steps on product rheology during scaleup cannot be overemphasized. This investigation should take place early in product development, so that the processing variables can be complemented by formulation to achieve the desired end product properties. Too many times formulation is set before evaluation of a processing scheme is done, and an existing plant may have to be redesigned. Sometimes technology, when used intelligently, can produce a unique product never achieved on the bench. At the very least, the product formula and processing equipment can be dovetailed to achieve an optimized process on a least cost basis. To do this, however, one must know which of the numerous process variables are critical and how they should be changed to obtain the desired results.

It is sometimes possible to predict the behavior of an emulsion in the plant by fully analyzing its rheological characteristics. For example, if one runs a viscosity versus shear stress curve and finds that an emulsion has a yield point, is highly shear-thinning, and has a basically high viscosity even under shear, one can predict problems with gravity flow of this product through a pipeline. Similarly, if a product loses viscosity irreversibly under shear, one can expect viscosity losses due to transfer and filling operations. Just about any problem can be overcome with enough time and money, but these two are rarely in adequate supply. The best product in the world will not come to market unless it can be made economically and sold at a profit. The proper application of the fundamental processing steps of mixing, heating, cooling, shearing, and homogenizing in cosmetic manufacture will enhance the chances for success of any new product.

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