

Mixing fine emulsions

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Fine emulsions make excellent carrier systems for a wide variety of cosmetics and pharmaceutical active ingredients. Lotions, moisturizing creams, antiperspirants, shampoos and many other products acquire their effectiveness, elegant texture, and attractive appearance in large part due to the quality and stability of the emulsion system. Emulsions consist of two immiscible liquids; the component present in a larger amount is called the continuous phase and the second liquid is the dispersed phase. In a stable emulsion, the dispersed phase is suspended uniformly as discrete droplets throughout the continuous phase.

Big and small drops coexist in the emulsion and their size distribution gives the best description of the emulsion, affecting both stability and viscosity. By their very nature, emulsions are thermodynamically unstable and the two phases eventually separate. An emulsion that is considered to be “stable” will not change its aspect for an acceptable amount of time. Storage stability period can range from a matter of months or years, depending on the product end use.

In the cosmetics industry, the challenge of making high quality stable emulsions is often a moving target due to changing consumer tastes, market demands and product requirements which drive companies to create many new formulations or tweak existing ones. Each new product can bring with it a fresh set of challenges including optimizing the mixing operation. This article focuses on the role of mixing in emulsion preparation and presents a number of mixing design innovations that are revolutionizing the way some manufacturers produce cosmetic emulsions.

MIXING THE RIGHT CHEMISTRY

Agitation disperses the liquid molecules and generates the emulsion. Manually shaking a bottle of water and oil, for instance, will produce droplets visible to the naked eye. By increasing the level of shear and agitation, it is possible to achieve much smaller droplets, ideally in the submicron or nanom micron range.

Because the phases in an emulsion are immiscible, the dispersed droplets will eventually combine and form a separate liquid layer. Chemical surface active agents, also called surfactants or emulsifiers, are added to the formulation to keep the discrete droplets from coalescing long after the agitation step.

Therefore, for emulsification to take place and remain stable, the right chemistry and sufficient mixing energy are both required. Generally, the higher the shear put into creating the emulsion, the finer the droplets produced, and the more stable the emulsion. This trend is relatively consistent in most emulsions, no matter the end use or application. However, there is no ideal droplet size that applies to all formulations. In other words, a 0.5-micron average droplet size may be considered stable for one emulsion but not for another.

Another consideration is the property of some emulsions to collapse when exposed to extreme shear. Such shear-sensitive emulsions achieve stability within a window of mixing intensity, requiring high shear to form stable droplets of the dispersed phase but not too high a shear as excess energy causes the droplets to coalesce.

In reality, many other factors apart from shear input affect emulsion stability including inherent chemical and physical properties of the dis-

persed phase and the continuous phase, volume phase ratio, emulsifier choice and concentration, thermodynamic changes during emulsification (reactions, heat transfer), method and order of addition, etc.

TRADITIONAL EMULSIFICATION METHODS

Rotor/Stator Mixers

Throughout the cosmetics and other process industries, high shear rotor/stator mixers are widely used for emulsion preparation. Available in either batch (top-entering) or inline (continuous) configuration, these mixers are comprised of a rotor that turns at high speed within a stationary stator (Figure 1). As the blades rotate, product is continuously drawn into one end of the mixing head and expelled at high velocity through the openings of the stator. The differential speed and close tolerance between the rotor and stator generate high levels of hydraulic shear, promoting fast mixing and producing small droplets in emulsions. Rotor tip speeds between 3,000 to 4,000 ft/min (914-1220 m/min) are typical.

A batch rotor/stator mixer is sized according to the volume of the mix vessel to ensure adequate flow. It can be used

as a stand-alone tank-mounted or portable unit for products up to around 20,000 centipoise (cP). When used in combination with other agitators, the viscosity range can be extended to several hundred thousand centipoise.

For example, multi-shaft mixers composed of three independently-driven agitators are commonly used in the production of viscous cosmetic creams (Figure 2).

A high speed saw-tooth disperser quickly draws powders into the liquid through a powerful vortex while the rotor/stator breaks down any solid agglomerates, produces fine droplets and homogenizes the entire batch. At the same time, a low-speed anchor agitator promotes bulk flow, feeds fresh product to the high speed blades and ensures uniform batch temperature by constantly scraping the vessel sidewalls and bottom. The versatility of this mixer system allows it to

accomplish a range of operating conditions for a specific application and can also handle a number of different applications. In fact, many multi-shaft mixer installations in the cosmetics industry are being used to develop and produce a full line of cosmetics and personal care products. In this type of mixer, shear levels and flow patterns are easily fine-tuned, making it possible to produce gels, night creams, toothpastes, moisturizers, after shave balms, facial masks and liquid make-ups in a single mixer.



Figure 1 – Rotor/stator assembly of a batch high shear mixer.

On the other hand, an inline rotor/stator mixer is used in a truly continuous mode, where it is sized according to the desired flowrate, or in a recirculation loop connected to virtually any size batch tank. It's not uncommon for large gently-stirred vessels to incorporate an external inline rotor/stator.

In an inline mixer, the greatest extent of droplet size reduction occurs within the first few passes. This phenomenon is true for almost any emulsion. Past this stage of sharp decrease in droplet size, the emulsion hovers at an equilibrium size despite subsequent recirculation. The same trend applies to batch rotor/stator mixing systems although the actual number of product turnovers is not as easy to define. It is always useful to know the point at which droplet size is already in equilibrium in order to avoid over-processing.

Over-processing not only unnecessarily consumes time and power, but also raises product temperature which could cause droplets to recombine or induce an irreversible change in emulsion viscosity.

High Pressure Homogenizers and Colloid Mills

If the equilibrium droplet size achieved in a conventional rotor/stator is larger than desired, manufacturers are forced to add more surfactant and/or switch to higher energy devices such as high pressure homogenizers and colloid mills.

Homogenizers use high pressure energy to break droplets and particles present in fluids by forcing the product through a narrow-gap valve into a lower pressure environment. The pressure gradient across the valve and the resulting turbulence and cavitation all contribute to the intensity of emulsification.

Whereas rotor/stator mixers allow the emulsion components to be combined, mixed and finished in a single vessel, high pressure homogenizers require a 'pre-mixer' to combine raw materials into a rough emulsion. If solids are present in the emulsion, these must be broken down to some extent prior to homogenization to prevent clogging and other operational problems. Another drawback to high pressure homogenization is the fact that it generates a significant amount of heat, usually requiring pre-cooling of both the machine and the rough emulsion feed to mitigate. Most systems also require intensive cleaning after runs to keep the unit sterile and to prevent



Figure 2 – Multi-shaft mixer equipped with three independently-driven agitators: a high speed disperser, a rotor/stator mixer and three-wing anchor agitator.

cross-contamination between different batches. These systems are comparatively expensive, entail high energy consumption and typically require a large footprint. Homogenizers have well-proven capabilities in emulsion production but there is a strong case for cosmetic manufacturers to explore other viable methods and technologies.

Colloid mills, on the other hand, are essentially rotor/stator type devices. Many design variations exist but a typical colloid mill configuration consist of a conical or disk rotor and a stator; each piece features complementary grooves that serve as channels for

the emulsion fluid to flow through. A gap or spacer ring maintains a close tolerance between the rotor and stator. As the rotor turns at high speeds, emulsion fluid is pumped between the rotor/stator surfaces and the hydraulic shear forces generated in the gap produce fine droplets.

Colloid mills are simpler to operate and consume less power than homogenizers though certain models are also labor-intensive and time-consuming to clean. Their main disadvantage however is the relatively small volume of product that can be emulsified in a given time. This low throughput forces many manufacturers to install multiple colloid mills in parallel, each requiring separate cleaning and maintenance.

NEW ALTERNATIVE: ULTRA-HIGH SHEAR MIXERS

New developments in rotor/stator technology present a number of viable alternatives to traditional emulsification equipment. Called "ultra-high shear mixers", these new devices deliver more vigorous mixing and greater throughput compared to conventional rotor/stator mixers and colloid mills. When utilized as a pre-mixer installed prior to a high pressure homogenizer, an ultra-high shear mixer can reduce the number of homogenizer passes required to reach the final droplet size. In some single pass requirements, the ultra-high shear mixer can eliminate the homogenizer entirely, delivering higher throughput while requiring less maintenance.

Batch Ultra-High Shear Mixer

The Ross PreMax is a top-entering batch mixer

equipped with a patented "Delta" rotor/stator assembly (Figure 3). The rotor is specially contoured for high pumping capacity and shear intensity. Product is drawn from above and below the mix chamber and expelled radially through the stator slots at high velocity. This generates upper and lower vortexes allowing for extremely efficient powder additions and rapid turnover rates. Very fine droplet sizes are achieved while solids are quickly wetted out instead of floating



Figure 3 – PreMax Batch Ultra-High Shear Mixer with "Delta" rotor/stator (US Patent No.6,000,840) capable of tip speeds up to 5000 ft/min (1524 m/min).

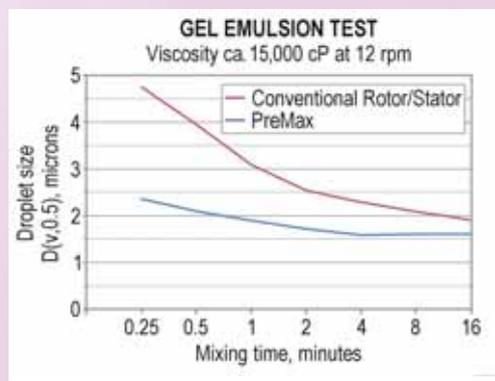


Figure 4 – Comparison of droplet size reduction performance. The graph shows droplet size curves for a cosmetic gel emulsion prepared on a conventional high shear rotor/stator mixer and on the PreMax ultra-high shear mixer.

on the liquid surface. The PreMax is typically used as a stand-alone unit and does not require supplemental agitation for products up to 50,000 cP.

For higher viscosity products, it can be used in combination with an anchor agitator in a multi-shaft mixer arrangement.

Users that have switched from a regular rotor/stator mixer to the PreMax experience a significant impact on production time. In side-by-side tests, the PreMax has also been shown to produce low-viscosity and high-viscosity emulsions up to six times faster than a conventional high shear mixer (Figure 4). In some formulations, including cosmetic gels and creams, the average droplet size was smaller in the samples prepared in the PreMax.

Inline Ultra-High Shear Mixers

Even more aggressive ultra-high shear mixers are available in inline (continuous) configurations. These include the Ross Series 700 mixers with three rotor/stator options, namely: the X-Series, QuadSlot and MegaShear – see Figure 5 for detailed descriptions of each design.

Running at tip speeds as high as 11,000 ft/min

shorter cleaning time equates not only to a faster changeover procedure but also to longer intervals between cleaning cycles (longer production runs).

In a typical set-up, a batch mixer is used to combine the raw materials and the resulting rough emulsion is then passed through the inline ultra-high shear mixer. More challenging formulations require multiple passes and due to the intense

gineered rotor/stator produces a very fine emulsion premix, reducing the number of passes through the high pressure homogenizer and lowering the risk of clogging.

This multi-stage emulsification process offers substantial benefits in terms of improved throughput and maximized utilization of the high pressure homogenizer.

Another typical processing set-up involves a multi-shaft mixer equipped with an anchor agitator, high speed disperser and regular rotor/stator. This system is used to combine all raw materials of a viscous cosmetic emulsion.

Towards the end of the mix cycle, the product is fed into an inline ultra-high shear mixer and recirculated a few times to finish the emulsion and achieve the target size distribution.

Depending on the formulation, this 'polishing' step can also be done at the start of the cycle, i.e. the base emulsion is subjected to intense mixing to establish the desired droplet size, followed by gentle agitation to incorporate other ingredients and complete the final product.

CONCLUSION

Equipment selection is a matter of balancing cost, system capability and product requirements. With a broader variety of emulsification equipment available today, manufacturers can now implement a lean production system that truly meets both their process-line needs as well as their business needs – all at a lower cost than what the same process would have required just a few years ago.

The challenge of finding the right equipment can be simplified by partnering with an experienced supplier and performing simulation trials. Process engineers are encouraged to explore these new technologies as part of a creative strategy to boost competitive advantage.

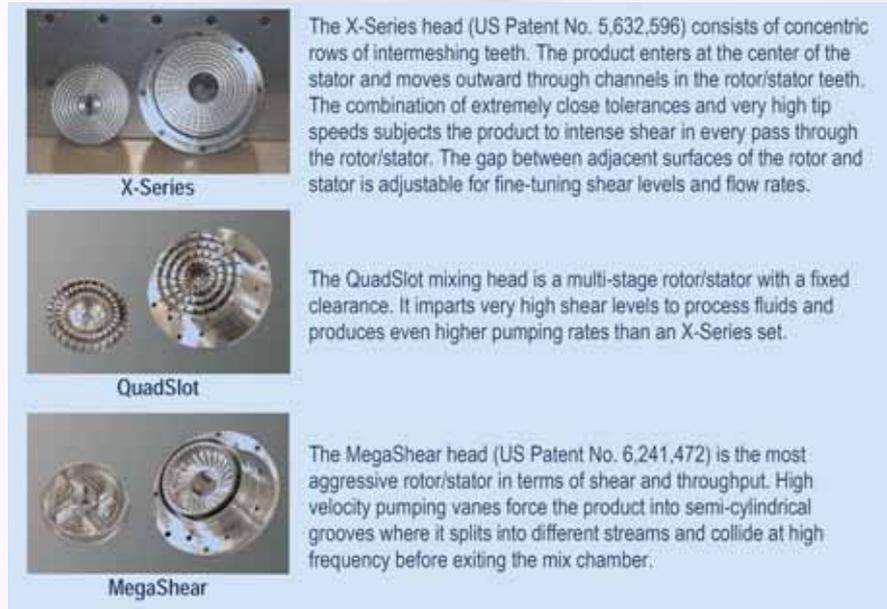


Figure 5 – Inline ultra-high shear mixers.

(3353 m/min), a Series 700 mixer is capable of far greater flowrates compared to a similarly-sized high pressure homogenizer or colloid mill. In many applications, it is more effective at reducing droplet size. Manufacturers that find this to be true for their particular formulations welcome the change because of the associated issues in maintaining and cleaning high pressure homogenizers and colloid mills. By comparison, the Series 700 mixers are easy to clean and disinfect in place. Based on user experiences, the

energy imparted to the product, temperature must be closely monitored.

Users also benefit from the flexibility of this device in terms of capacity – a Series 700 mixer can process production-size volumes as easily as it can handle pilot-scale or R&D batches.

Multi-Step Emulsification Processes

In cases where ultra-high shear mixing does not necessarily eliminate homogenization its utility as a 'pre-mixer' is still significant. The specially en-

