Improving Cosmetic Formulation Quality Through Innovative Processing Technology: Preparation of MicroDroplet/Particle Master Batches through Innnovative Compounding Techniques

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Essentials and Flaws of Conventional Successful Cosmetic Emulsion and Paste Processing: Pros and Cons

The intimate, uniform and lump-free mixing of a formulation containing two or more fluid components, one being lipophilic and the other hydrophilic, with or without the addition of powdered solids, to form a stable emulsion is a complex process.

Successfully preparing such cosmetic systems, including lump-free pastes and creamy lotions, is more of an art rather than a science. Cosmetic componders and Cosmetic and Personal Care technoloigsts, wether at the lab bench or involved in scale up and full scale manufacturing, guard their technology as as a highly valuable secret , because in Cosmetics R&D, it may take investigations virtually thousands of combinations and variations of ingredients and process parameters to succeed in preparing stable, high quality concentrates of a useful master batch and it often may even take several years to optimize the resulting recipies.

McCutcheon's Emulsifiers & Detergents© catalogs (The Manufacturing Confectioner Publishing Co.) presents an insight into the tremendous knowhow needed to succeed in this field, alone from a surface-chemistry point of view. Literally thousands of surfactants/emulsifiers are available to both, the highly skilled and advanced, as well as the more junior formulator, seeking to optimize a seemingly endless variety of required parameters.

In addition to the optimal ingredients of choice, the cosmetic compounder and emulsion formulator, in conjunction with pilot and full scale manufacturing experts, needs to select the proper mixing equipment for specific scales of operation, to generate the desired properties, such as droplet size, droplet and particle size distributions, rheological behavior, stability at room and elevated temperatures, as well as after freeze thaw tests etc..

The resulting choice of equipment will profoundly influence the desired endproperties of the manufactured product. Other contributors to final product quality include freedom of contamination through abrasion from the equipment walls, attained uniformity of composition, viscosity at selected shear rates, color, sensory properties for topical application, desired rheological behavior, such as thixotropy, dilatancy, yield stress, smoothness, tackiness, and of course, stability over time, both during the processing itself as well as following manufacture, the so-called shelf-life. Especially important items for the manufacturer to look out for during the production process, are the contributors to rheological, Newtonian or non-Newtonian behavior and time dependent stability.

Yet other areas of great importance to the successful processing of cosmetic emulsions include sequence and timing of ingredient additions, temperatures to be maintained, pH control and most importantly, the volumetric uniformity of adding emulsifiers and other tensides in selected internal and external phases prior or during processing.

The extremely high degree of uniformity and homogeneity of the mixture are one of the most important properties to be attained in cosmetic products and result from optimal emulsification and dispersion of all the ingredients in cosmetic processing. Selecting and properly operating the correct processing machinery in the course of manufacturing the product, is of equal importance as that of selecting the proper additives, vehicles, binders and insoluble ingredients. Obtaining a maximum of uniformity and homogeneity is not an easy task, demanding from the manufacturers a fair knowledge of the principles of rheology, tribology and fluid dynamics.

One of the difficulties in obtaining the above described rheologic and dispersive product qualities, is the little known existence of a fluid dynamic barrier to efforts of comminuting droplets and particle agglomerates below the size of approximately 10 to 30 μm, defined in the literature as the "smallest Kolmogoroff eddy diameter". This

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Fig. 1: A three roll mill in a shipping crate

Fig. 2 and 3 show a three roll mill in operation

fluid dynamics phenomenon was first described by the Russian scientist Andrei Kolmogoroff (Kolmogorov, Andrey Nikolaevich) in "Dissipation of Energy in the Locally Isotropic Turbulence" (Proceedings of the USSR Academy of Sciences 32:16-18). According to Kolmogoroff, eddies in stirred liquids cannot be made smaller than say 15 micrometers in the case of aqueous or alcohol solutions, regardless of shear rate, rotor rpm or horsepower input into the stirring process. This means, on such a small scale, total mixing uniformity cannot be obtained with ordinary commercial equipment.

For processing pastes and thick slurries, typical compounding machines for lab scale include kitchen mixers, Hobart bowls and for and larger batches, three-roll mills, two-roll mills, single-screw and twin-screw compounders. Examples are shown in Fig. 1 to 3.

The three-roll mill, frequently applied in the preparation of cosmetic formulations, uses the shear force created by three horizontally positioned rolls rotating at opposite directions and different speeds relative to each other to mix, refine, disperse, or homogenize viscous materials fed into the nip of the first two rolls.

One of the major problems with three-roll mills is the progressive accumulation of larger particles and hard agglomerates in the space immediately above the nips of the rollers. Such segregation impairs product uniformity and can cause product contamination with small amounts of abraded material from the rollers' surfaces.

Conventional mixing in agitators and their propellers, as shown in Fig. 4 and 5, cannot achieve the micro-uniformity required in high quality cosmetic products, when blending liquids of widely different viscosity, disintegrating and solubilizing solids, creating highly uniform and fine emulsions or suspensions, and dispersing active ingredients and rheology modifiers.

Fig. 4

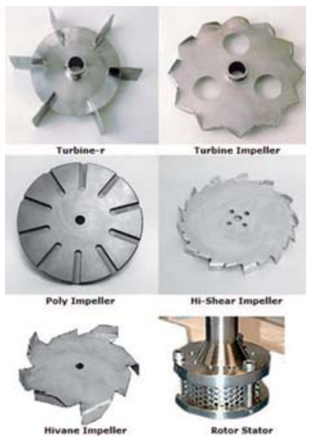

Fig. 5

Fig. 4 and 5 show a typical conventional agitator and a variety of agitator blades

Mixing powders in high concentrations into liquids is one of the major challenges in the personal care, pharmaceutical, biotechnology and cosmetics industries. Process temperature and mixing times must be kept to a minimum. Rheology modifiers, such as natural gums, thickening agents, such as Methocel® and emulsifiers, easily form lumps when added too rapidly to the stirred liquid in the vessel. The subsequent delumping is a difficult and highly time consuming process, often exacerbated by operator errors, such as adding the powder too quickly. In many cases the agglomerated materials will never attain complete emusion/dispersion homogeneity.

However, agitators, like the one shown in Fig. 4, do not produce sufficient shear at the immediate peripheries of the suspended "micro- and nano-lumps" and therefore are unable to break them up. New and improved technologies must be developed, capable of shearing apart such small lumps, even in the sub-micron or nanometer size ranges.

Measuring the particle size distribution before and after processing of a cosmetic paste or cream would easily reveal the best processing method for the task at hand, although it may not be easy to perform it in the sub-micron or nanometer size range as optical light microscopy cannot be used when observing the non-transparent surface of a paste and because the particle sizes of interest, even if separated from the vehicle, would be below the wavelength of white light. Only Atomic Force Tunneling Microscopy can be used for this task. This method is illustrated in Fig. 10.

Innovative Compounding of Highly Viscous Pastes with High Particle Loading

To improve the understanding of and to show the need for more ground-breaaking improvements and innovation in the processing of "low and sub-micron master batch emulsions and pastes," the author has developed a novel processing technology, the Holl-Reactor™, in which emulsions, useful for cosmetic creams and lotions, can be prepared. In this novel technology, coarsely premixed thin films of the mix components are subjected to high, intense and continuous shearing between parallel flat surfaces, only less than 300 µm apart, one surface being stationary and the other moving fast, in Fluid Dynamics called "Couette Flow", has a number of significant benefits. For example, internal phase concentrations of about 50% can be produced in a flow-through process having low viscosities (i.e. about 5 cP). Droplet size of about 2 microns and finer have been demonstrated. Near translucent systems are easily attained by the process.

While the choice of optimal emulsifiers and concentrations are dependent on the lyophilic component or oils to be emulsified, and to some extent are held as proprietary for individual systems, we present below just one example of such a system. In this system, Jojoba oil served as the internal phase with water as the external phase. The emulsion composition is described below. Such systems are stable for months to years under ordinary storage and use conditions.

The composition of the experimental 50:50 Jojoba-water emulsion:
43 gram Jojoba oil
50 gram de-ionized water
0.2 gram sodium dodecylbenzene sulfonate

The emulsion preparation process involved dissolving 0.2 g of sodium dodecylbenzene sulfonate in de-ionized water and pumping it through the Holl-Ergatron™ emulsicator at a metered flow rate of 25 ml/min through a first feed line A while simultaneously feeding the Jojoba oil through a second feed line B at the same flow rate of 25 ml/min. Within only less than 3 seconds flow-through processing time (residence time), a stable emulsion was obtained as shown in Fig. 6 and Fig. 7.

Fig. 6: A Holl-Ergatron™ emulsicator during production of a 50:50% experimental Jojoba-water emulsion

Fig. 7: A close-up view of the 50:50 experimental Jojoba-water emulsion

A schematic section through the Emulsicator™ of Fig. 6 and its processing principles is presented in the following Figure 8.

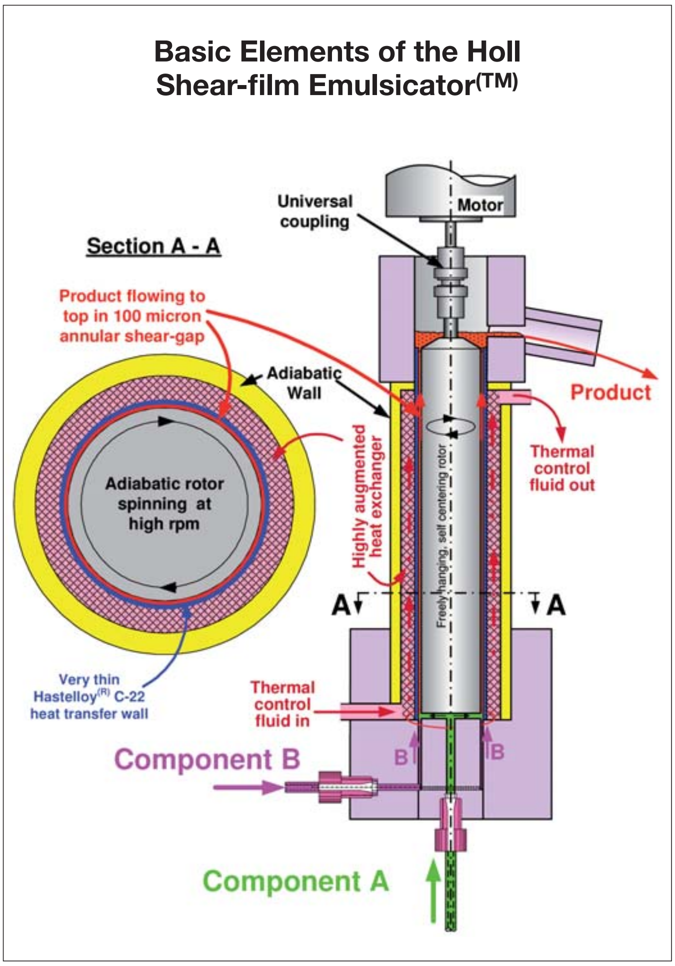

Fig. 8

Uniformity of Composition

A different set of problems in cosmetics processing to be overcome is the attaining of uniformity of composition in stiff cosmetic pastes forming precursors to such products as lipsticks and similar products.

In the search for a more effective uniformization method for stiff pastes, a test procedure had to be developed where sub-micron or nanometer size carbon black test particles are admixed in small amounts to a highly viscous, almost dry and dough-like paste of an experimental composition of bright white color. and in Fig. 9:

The task was to admix as uniformly as possible 1.0 g of carbon black to a 250 gram batch of a lumpy mixture of 99.96 % pure Ceralox APA 0.5 white aluminum oxide powder of average particle size below 300 nanometers to a a small amount of a viscous and tacky binder material, to form a pre-mix.

No detectable, visible trace of carbon black particles or any of their agglomerates or aggregates was found after completing the innovative mixing process, described in more detail in the paragraph below, evidencing the unusual effectiveness of the procedure as described below.

To eliminate contamination from wall abrasion of a possible mixing chamber, mixing was performed using only two round, flat and abrasion resistant UHDPE platens of 10 inches diameter by ½ inch thick and a 40 ton hydraulic press.

The raw and lumpy pre-mix to be compounded was sandwiched between the two platens and placed near the center, as shown in Fig. 9. The "sandwich" with the lumpy mix in the center was then loaded into the 40-ton press and "press-squeezed" until the sandwiched lump of paste grew radially into a 2 mm thin, rather dry and crumbly "pizza" of about 10 inches diameter. (Fig. 9)

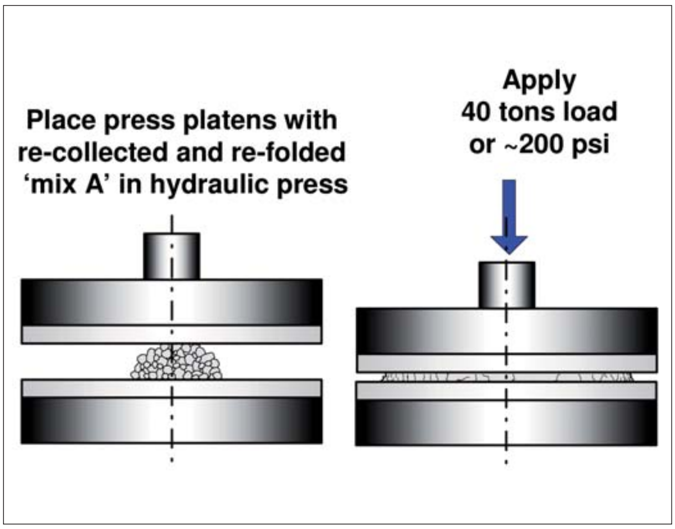

Fig. 9

Thereafter, the "pizza" was peeled away from the platens, balled up into a new lump and placed again in the center of the platen-sandwich to be subjected to the same process of press-squeezing as described before. This process cycle was repeated ten times whereupon the "pizza" assumed the surprising appearance and consistency of a thin sheet of rubber whose edges showed no cracking and upon flinging it back and forth by hand in the air, it never broke up or tore. The engineering term for this "pizza's" rubbery property is called "superplasticity."

After ten re-collecting and re-folding cycles of the above Press-mixing™ procedure, the added 1.0 gram of carbon black powder with average particles from 8 to 100 nanometers were absolutely uniformly dispersed throughout the >250 g batch, confirmed by using atomic force microscopy (See Fig. 10).

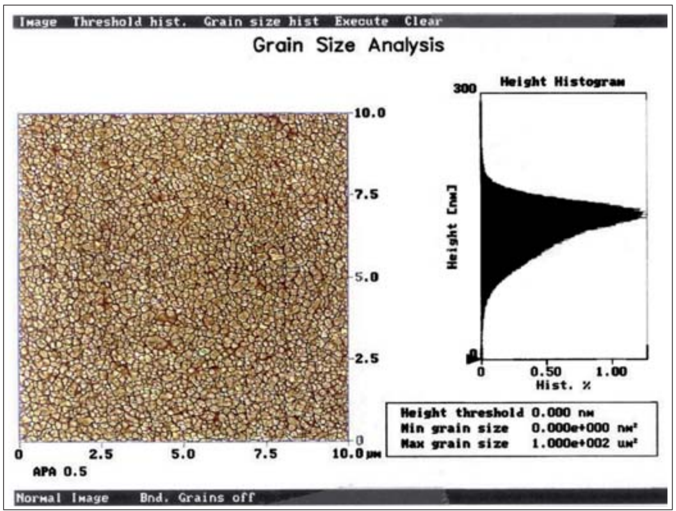

Fig. 10: The above micrograph in Fig. 10 shows the AFM result of the pressmixed™ aluminum oxide paste with a very small amount of carbon black uniformly distributed on a nanometer scale

Industrial scale production of cosmetic products require the "press-mixing" to be modified and adapted to become a mechanized batch or semi-continuous process with easy to control rotary elements but retaining the high shear effects of the pressmixing.

Fig. 11 and 12 show the principle of achieving nanometer scale paste mixing using another effective method of contamination-free paste shearing between non-metallic surfaces when rotating a solid, non-metallic cylinder eccentrically inside the mix containing cylindrical vessel (US Patent 6,752,529, Inventor Richard Holl), a method which best can be described as "Boundary Layer Milling™."

A brief description of this novel technology's fluid dynamics' base is now provided to enable the reader to understand the distinctions between the author's new approach and the prior art of paste processing. According to chemical engineering principles of fluid flow in pipes, such flow generally has most of the volumetric flow varying in velocity from a maximum in the pipe center to a minimum near the wall. The flow above a certain Reynolds Number is called turbulent when away from the wall and laminar in close proximity to it. Certainly, turbulence is a recognized significant element in tearing apart internal phase liquids in emulsions, or agglomerated particulates when preparing desirable cosmetic or personal care dispersions.

Besides the main volumetric, turbulent flow, there is always a thin region adjacent to a pipe or tank wall, called laminar boundary layer, with energetic molecular mixing motion that varies in intensity from highest, far away from the wall to a minimum as one approaches the wall. It is this boundary layer zone near walls that is at the heart of the Boundary Layer Milling Technology. If one envisions a rotor and stator (like in Fig. 11) where the rotor moves at high rotational velocity and the gap between the rotor and stator is designed to be approximately less than one mm thick at their closest approach, then fluids pumped through such a device will be sheared in a thin film at enormously high local shear rates where rotor and stator walls are at a minimum distance. Using this "Boundary Layer Nanomilling" approach, the less than efficient, classical turbulence mixing method of other emulsifying systems is avoided, while the manufacture of much higher quality products can be expected.

One of the advantages of such a system design is its substantially lower cost compared to existing systems, as well as being a continuous process, for laboratory or scaled up applications.

The use of effective "Boundary Layer Milling" to obtain cosmetic emulsions of high quality and stability can be carried out in yet another vertical arrangement of a rotating, cylindrical element whose peripheral surface is shearing the emulsion ingredients against a stationary inner cylinder wall, called a stator. The instrument is called "Ergatron™" in the marketing literature and is operated under license at various locations in the US and Europe under US Patent 7,780,927. When used as an emulsifying processor, it can be operated continuously with temperature and pH control (Fig. 6). If required, shear rates of over 200,000 /sec can be achieved.

Fig. 11

Pressmixing™, "Boundary Layer Milling" and Nanomilling™ are terms used in the present article for the novel processes described of continuously preparing ultra-fine, low viscosity, high internal phase concentrates and dilutions thereof for lab, pilot and full scale manufacture of novel creams, lotions and "nano-pastes."

The described new processes have the potential of greatly improving quality, economics and profitability in cosmetic and related healthcare business areas. They hold great promise as true breakthrough technologies, capable of displacing conventional methods in overcoming the tough technology barriers associated with continuous and uniform processing of highly viscous, multi-component products for future markets.

Fig. 12