Surfactant-Free Formulating

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Abstract

The author describes how familiar hydrophobic materials can be formed into stable aqueous dispersions via an extraordinary high pressure, high shear process utilizing blends of alkylated phophatidyl choline.

The era of modern cosmetics emerged in the 1940s with the widespread use of synthetic surface-active agents. These materials, commonly called surfactants, modified the surface tension of the oil and water phases and enabled formulators to mix them together in order to form a composition that was stable for at least the commercial shelf life of the product. These preparations were called emulsions, and the surface-active materials used to form them were emulsifiers.

Such emulsions are generally prepared by heating the oil and water phases to a temperature of 70°C or greater before combining them. The oil and water phases are mixed together until uniform, then slowly cooled to ensure the formation of the appropriate-sized droplets or micelles, which control the stability of the emulsion. The emulsions typically have a homogeneous, opaque, white appearance and a smooth, pleasant feel upon application to the skin, hair or other epithelial surface. In fact, emulsion chemistry has become a major disciplinary area that a competent cosmetic chemist must master.

However, the introduction of surfactants to the cosmetic industry may have been a double-edged sword, because although surfactants have yielded cosmetics with desirable aesthetic properties, they have also created issues associated with their use. To the formulator, developing emulsion-based products may be problematic. The sometimes time-consuming process can be incompatible with key actives. They can limit aesthetic properties, cause thermodynamic instability and yield non-reproducible results. Additionally, some formulators find scale-up for manufacturing difficult. Surfactants can also be skin irritants. They strip the lipid barrier of the skin or the lipid bilayer of epithelial cell membranes, leaving the tissue vulnerable. Occasionally, surfactants themselves can evoke adverse skin reactions.[1-9]

Surfactant Alternatives

Given the risks and faults, it is easy to understand a formulator's desire to find an alternative to conventional emulsion systems. Ideally, the formulation would have the same or improved aesthetic properties and would be prepared without the use of traditional surfactants and emulsifiers. But, where can such a system be found? What means can be employed that will allow two immiscible substances to mix? The answer to these questions may lie more in physics than chemistry. Familiar hydrophobic materials (such as oils, waxes and silicones) can be formed into stable aqueous dispersions via an extraordinary high pressure, high shear (HPHS) process that utilizes unique blends of alkylated phosphatidyl choline.

Molecules of phosphatidyl choline and certain other phospholipids will spontaneously form assemblies with one another in water at extremely low concentrations. These assemblies are typically bi-layers with the polar head group of the molecule interacting with the external and internal aqueous phase. Concurrently, the non-polar aliphatic portion of several molecules interact with one another or with a non-polar fluid to form the bi-layer.

Phosphatidyl choline (PC) can form up to 11 different assemblies in water depending on the alkyl groups present, the phase transition of the molecule, the concentration of PC present, the temperature of formation, and the shearing energy applied during formation. Some of these assemblies are more thermodynamically stable than others. Typically, assemblies formed above the transition temperature of the phospholipid form more stable assemblies because of the greater energy

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present. However, assemblies often transition to a less stable assembly as the system is cooled. Blends of phospholipids generally form more stable assemblies probably due to the synergistic packing of the phospholipids. Ideally, if one could introduce energy without the use of heat, then it would be possible to form more stable assemblies. One of these is the lamellar assembly.

High energy at low temperature can be achieved by exposing phospholipids to extremely high shear under extreme pressure. High shear is achieved by diverting the fluid into two channels that impinge upon one another in a chamber at velocities approaching 500 m/sec. Further, the shearing action takes place under pressures ranging from 10,000 to almost 50,000 psi. The expansion of the fluid returning to atmospheric pressure upon exiting the chamber causes an ultra-efficient break up of the hydrophobic material.

Under the right combination of shear and pressure, enough energy can be imparted to allow almost instantaneous formation of even the most complicated phospholipid assemblies. Since the formation process is almost instantaneous, the amount of time that the process media needs to be exposed to shear and pressure can be very short. This duration is so short that the assemblies formed do not have time to disassemble before they are no longer exposed to the shear and pressure conditions used to form them. By employing this procedure, lipophilic materials can be incorporated into an otherwise all water based product.

Fluid Lamellar Phase

The most important state in which the phospholipid assembly can exist is the fluid lamellar assembly. The most stable phase is the L_α (also known as the liquid crystalline phase).This phase is only possible above the gel-to-liquid crystalline transition temperature energy level of the phospholipid or mixture of phospholipids used. Below the transition temperature, the assembly exists as a less stable, $L\beta$ phase (also known as a gel phase). Pure phospholipids have a lower transition temperature than mixtures of similar phospholipids.

The L_α phase has two phopholipid assembly species that can form. The first species is the usual unilamellar layer or the multilamellar phospholipid bilayer with its large regions of water between bilayers. The second species is a reversal that occurs as the amount of lipophile is increased in the presence of water. Here, the lipophilic tails extend into the oil and areas of water separate the hydrophilic heads. The amount of lipophile that can be accommodated into a stable, water-miscible dispersion can be greater than 50% by weight.

Different lipophiles vary in their ability to be incorporated into an L_α phase. Generally, non-polar lipophiles can be incorporated much more easily. Higher purity lipophiles will usually be capable of incorporation at higher levels. Most non-organically modified silicone derivatives can be incorporated at levels from 30% to greater than 50%. The critical aspect of the production of the stable L_α phase dispersions is processing at low temperatures, but with high energy. The process used must exceed the transition temperature energy level without actually reaching the transition temperature.

The L_α phase assembly must be completed in a fraction of a second, and the conditions that allowed the assembly to form must be removed immediately after the assembly is complete. The result is a stable dispersion of high concentrations of lipophiles that can be indefinitely dispersed in water or water-based products. Typically the particle size of the micelles created will be from 100 to 500 nanometers (nm). This is about 1/10 to 1/50 the size of particles produced by standard emulsification techniques. Further, HPHS processing is so efficient that the distribution of particle sizes for the micelles is extremely tight.

Viscosity enhancement: One of the most interesting aspects of the L_α phase dispersions made by high shear high pressure processing is the effect on viscosity. Typically, any stable emulsion containing 25% or higher of petrolatum will have a viscosity measuring more than 100,000 centipoise (cP). A high shear, high pressure processed dispersion of 25% petrolatum in water will have a viscosity of less than 400 cP and can be sprayed by a finger-actuated pump spray.

This difference is entirely due to high shear, high pressure processing. A formula containing 50% petrolatum processed by high shear and high pressure is a stable lotion with a viscosity of approximately 4,000 cP. The exact same formula made by conventional homogenizing mixing has an initial viscosity of 360,000 cP and is not stable at room temperature for more than seven days. This is due to the lack of water binding to the surface of the micelle formed by HPHS processing. This explanation is confirmed by Differential Scanning Calorimetry, which shows no thermal breakdown of the surface-bound water, as is seen in standard emulsions.

Further, HPHS processing imparts a negative charge, or zeta potential, on the surface of the micelle that repels them from neighboring micelles. Therefore, the hydrophobic particles are free to move past one another, creating a fluid environment. High molecular weight dimethicones of 60,000 cP and higher have an excellent skin feel but have a viscous, honey-like texture that makes them difficult to incorporate into a cosmetic or pharmaceutical composition.

A 30% L_α phase dispersion of the same ingredient is a thin liquid that is completely water dispersible. These dispersions can sometimes provide a method to incorporate ingredients that do not lend themselves to any conventional emulsification system. It is possible to make stable 30-50% L_α phase dispersions of fluorinated materials such as polytetrafluoroethylene and perfluoropolymethylisopropyl ether. These dispersions can be further diluted in water. Neither of these two materials is considered to be emulsifiable by conventional means.[a]

L_α dispersions can be made with virtually any hydrophobe by carefully controlling the selection of phospholipids and the processing conditions during manufacture. One interesting property of these dispersions is that they alter the aesthetic properties of virtually all materials, creating new sensations with familiar materials. Conventional materials such as petrolatum, lanolin, waxes and natural oils are given a new "life" and purpose. Since the micelles of each lipophile are made the same way, they are all independent of any surfactant and, because they have approximately the same particle size and negative surface charge, there is no tendency for the micelles to coalesce.

HPHS dispersions of various lipophiles mix readily without issue. In fact, a virtually infinite array of lipophilic dispersions can be mixed at any proportions without creating any instability in the final blend. Thus the common practice of balancing the hydrophilic and lipophilic emulsifiers (HLB), depending on the composition of the lipophilic phase, in the preparation of standard emulsion systems, is now obsolete.

Aesthetic properties: A series of L_α dispersions can be prepared that have a range of aesthetic properties from very light with no residual feel to very emollient with a noticeable and prolonged residual feel. This permits a spectrum of tactile sensations that can be mixed to create virtually any aesthetic experience. An arbitrary scale from 1 to 1000 can be established to describe the aesthetic properties of a given dispersion. Those having light, rapidly absorbing properties would be on the low end of the scale, while dispersions having more unctuous, long-lasting effects would be designated with a value at the higher end of the scale.

Other lipophilic dispersions could then be assigned intermediate values depending on the degree of tactile properties they demonstrate. For example, a low viscosity hydrogenated polyisobutene dispersion is assigned the number 100 for its light tactile impression and fleeting afterfeel, while a cetearyl alcohol dispersion is assigned a value of 900 because of its pronounced emolliency and noticeable, prolonged "waxy" afterfeel. Similarly, cylcomethicone, phenyl trimethicone, a higher viscosity hydrogenated polyisobutene, petrolatum, gelled silicone and gelled hydrogenated polyisobutene have assigned numbers of 200, 300, 400, 500, 600 and 700 respectively. The numbers are assigned strictly on the aesthetic properties that the dispersion possesses. Making a dispersion of a lipophile imparts a tactile perception that is difficult to predict.

Recently developed dispersions of grape seed oil, cottonseed oil, olive oil, mineral oil and cocoa butter have numbers of 250, 450, 650, 750 and 850 respectively. Mixing the dispersions[b] in a variety of combinations and at different ratios creates virtually limitless tactile properties. Because these dispersions modify the tactile properties of the final product into which they are added, they have been given the name "aesthetic modifiers," and "AM" is used as a prefix with the number. The aesthetic modifiers typically have a particles size of less than 1 micron and usually are processed with HPHS agitation until the particle size is less than 250 nm. All of the modifiers are dispersible in water. Table 1 is a chart that illustrates the effect of various aesthetic-modifying dispersions on the properties of the final product.

L_α dispersions of lipophilic performance materials can also be readily prepared. These materials provide the finished product with its functionality. Sunscreen agents such as ethylhexyl methoxycinnamate, octacrylene and homosalate can be incorporated into stable dispersions at levels from 30 to 50%. Similarly, retinoids, vitamin E (α-tocopherol), α-bisabolol, silicone, essential fatty acids and petrolatum can be made into stable dispersions to provide the product with anti-aging, antioxidant, anti-inflammatory, moisturization and skin protectant properties. These dispersions are completely compatible with the dispersions used to modify the aesthetic properties. This compatibility has been verified by the homogeneous nature of the dispersion blends and the maintenance of their original particle size indicating a lack of coalescence of the lipophiles.

Compatibility: Since all of the dispersions discussed thus far are made essentially devoid of traditional

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[a] *Note: Polyfluorinated materials are insoluble in any known solvent. Therefore it is impossible for the hydrophobic part of an emulsifier to intimately interact with the polyfluorinated material. Thus a stable emulsion is not possible.*

[b] *System 3 is a product of Collaborative Laboratories, Stony Brook, New York.*

Table 1: Properties of Aesthetic Modifying Dispersions

Aesthetic Modifier	Initial Feel	Absorbency / Playtime	Residual	Comments
AM 100	Very Light	Short	Low, Smooth	Increases opacity of final product. Oil-Free.
AM 200	Very Light	Short	Emollient with smooth afterfeel	Helps to reduce any tackiness in finished product. Imparts a matte finish.
AM 300	Light	Medium	Light, silky afterfeel	Helps to minimize tackiness in finished product. Provides “dry” emolliency to skin. the end feel
AM 400	Light but with	Medium	Emollient with slight tackiness Consider using AM 200 or AM 300 to	Use in products for normal-oily richer texture eliminate any tack. Increases opacity of final product.
AM 500	Rich	Medium	Slightly unctuous rub in with rich, slightly tacky afterfeel	Tackiness can be reduced with AM 200 or AM 300. Provides good residual feel.
AM 600	Elegant texture	Short	Emollient, silky afterfeel	Good moisture barrier. Ideal for sunscreens and waterproofing. Reduces tack and drag.
AM 700	Rich	Long	Unctuous, slighty tacky emollient afterfeel	Excellent waterproofing agent for sunscreens.
AM 800	Rich, heavy	Long	Unctuous, waxy afterfeel AM 300. Increases viscosity.	Tackiness can be reduced with AM 200 or
AM 900	Very rich	Very Long	Waxy	Increases opacity of final product. Adds body with elegant waxy afterfeel. Reduces tackiness.

surfactants, they are compatible with sophisticated delivery systems created for pharmaceutical applications. Liposomes, nanospheres, encapsulates and many other delivery systems maintain their integrity when mixed with L_α dispersions while these systems are rapidly disrupted by emulsifiers and other surfactants often making them valueless in the product.

The L_α dispersions are freely miscible with water and can be diluted if desired. This typically only makes them thinner. However, if the water is first thickened with a natural or synthetic rheological modifiying agent, such as a carbohydrate polymer or an acrylate polymer, then the addition of the dispersions creates a product that looks and feels like traditional emulsion systems. Depending on the amount of the thickening agent or agents used, the final form of the product will be a thick cream, a soft cream, a lotion, a serum or a low viscosity fluid.

L_α dispersions are compatible with virtually all water-thickening agents. Preferably, thickeners that have a thixotropic property, such as xanthan gum, and methacrylate polymers or copolymers, when combined with starches and/or magnesium aluminum silicates, permit the formulation of elegant finished goods.

If the final system is to be acidic or contain a significant amount of acids, such as alpha hydroxy acids, then the use of xanthan gum, sclerotium gum, hydroxethyl cellulose, magnesium aluminum silicate, carrageenan, and modified starches is recommended.

These thickened water bases should contain little or preferably no surfactant, which has the potential to perturb the stability of the surfactant-free dispersions. Water-soluble performance ingredients such as glycerin, vitamin C or herbal extracts can be added directly to the thickened aqueous phase. Products can be made that are indistinguishable from standard emulsion systems. More importantly, formulations with unique aesthetic and performance properties can be prepared that enhance the enjoyment for the customer while using the product. Formula 2 shows a sunscreen lotion made by mixing a dispersion of a sunscreen blend (Ethylhexyl methoxycinnamate (and) butyl methoxydibenzoylmethane), with three aesthetic modifiers in a thickened-water base.

Surfactant-Free Formulating

The preparation of surfactant-free formulas requires three parts: a thickened water phase, a selection of dispersions to produce the desired aesthetic properties and a performance material that gives the final product its functionality. The materials are combined concurrently or sequentially. Since the particle sizes of the lipophilic dispersions are already pre-established by the HPHS processing, they can simply be mixed into the thickened water phase with gentle agitation at room temperature.

Formula 1. SPF 15 Lotion

Formulation Ingredient	
Water (aqua) (and) hydroxypropyl starch phosphate (and) carbomer (and) acrylates/C10-30 alkyl acrylate crosspolymer (and) acrylates/vinyl isodecanoate crosspolymer (and) xanthan gum (and) Ceratonia siliqua gum (and) cyamopsis tetragonoloba (guar) gum (Moisturizing Base, Collaborative Labs)[a]	35.25 % wt
Deionized Water	17.75
Glycerin (and) water (aqua) (and) sodium PCA (and) urea (and) trehalose (and) polyquaternium-51 (and) sodium hyaluronate (Advanced Moisture Complex, Collaborative Labs)[b]	1.00
Water (aqua) (and) cyclomethicone (and) PEG-8 (and) phospholipids (and) polyphosphorylcholine glycol acrylate (Aesthetic Modifier - 200, Collaborative Labs)[c]	9.50
Water (aqua) (and) phenyl trimethicone (and) cyclomethicone (and) phospholipids (and) dimethiconol (and) polyphosphorylcholine glycol acrylate (Aesthetic Modifier - 300, Collaborative Labs)[c]	4.50
Water (aqua) (and) hydrogenated polyisobutene (and) PEG-8 (and) cyclomethicone (and) phospholipids (and) polyphosphorylcholine glycol acrylate (Aesthetic Modifier - 400, Collaborative Labs)[c]	11.50
Water (aqua) (and) ethylhexyl methoxycinnamate (and) butyl methoxydibenzoylmethane (and) cyclomethicone (and) phospholipids (and) Melissa officinalis (balm mint) leaf extract (Solarease II, Collaborative Labs)[d]	20.00
Phenoxyethanol (and) chlorphenesin (and) glycerin (and) methylparaben (and) benzoic acid (Germazide MPB, Collaborative Labs)	0.50
	100.00

[a] Viscosity control
[b] Moisturization
[c] Emollient
[d] Sunscreen
[e] Preservative

The rheological properties are mostly due to the presence of the thickening agents and are completely independent of the complex processing conditions required to make conventional emulsions. No heat or extraordinary processing conditions are required. More remarkably, these systems are much more stable than their emulsifier-based counterparts. The hydrated thickening agent(s) provide a matrix into which the L_α aesthetic and performance dispersions are imbedded. As long as the thickening agent maintains its integrity at various thermal conditions, the product will maintain its stability. Therefore, unlike emulsions, these dispersions can be thermodynamically stable indefinitely.

Advantages

Surfactant-free formulating has many advantages. The time from concept to the marketplace is dramatically reduced. Typically surfactant-free formulations can be prepared in 10-15 minutes which allows a formulator to prepare 30 or more prototypes daily. This acceleration in speed of formulation variation is amenable to the effective use of statistically-designed experiments.

The aesthetic and rheological properties of the product can be evaluated immediately. Greater flexibility and rapid formulation changes are possible. Additionally, the compounding of surfactant-free formulations is a cold process that readily scales to manufacturing conditions, therefore the need for multiple pilot batches to optimize the processing conditions is virtually eliminated.

Surfactant-free formulations have distinct advantages in manufacturing as well. The process conditions are uncomplicated and therefore labor, overhead, and processing time can be reduced. This results in plant capacity increases without any additional capital investment. No heating and cooling is required, thereby increasing energy savings.

There are fewer materials to compound, and no sub-phases are required and it is much easier to insure batch-to-batch reproducibility. There is little waste, and little "rework" of a batch is required. Kettle dwell time is greatly reduced, and the product can be transferred directly to the filling line once ingredient additions are completed. In fact, continuous processing is possible. Finally, the ease of manufacturing enables the product to be made exactly the same in any location in the world.

Perhaps most importantly, the consumer benefits from the use of surfactant-free formulations. The L_α-based systems are potentially more efficacious and less irritating. The integrity of liposomes and other delivery systems is maintained since the L_α -based systems are essentially surfactant-free. This permits the optimal penetration of the desired physiologically active ingredients, while retarding the penetration of unwanted materials.

Surfactant-free formulations have other interesting properties that enable them to serve as the ideal vehicle for various cosmetic and pharmaceutical products. The use of surfactant-free formulas typically provides lower penetration of the vehicle components into the skin and consequently irritation is reduced. When applied to a surface like hair or skin, the lipid barrier is not compromised.

Because of the low penetration, the uniformity of the resulting film allows for an even distribution of the active at the skin’s surface. This property is readily confirmed when the sunscreen formulation in Formula 1 is evaluated for its ability to block ultraviolet radiation. The SPF value of this formulation is 16.7 compared with an SPF of 8.9 for a conventional surfactant-based emulsion containing the same level of sunscreen. Since no surfactant agent is present, the vehicle does not’“wet” the surface. Therefore the surfactant-free formulation is essentially waterproof whereas the conventional emulsion vehicle is not, and, in fact, would require the addition of supplemental waterproofing agents to achieve this effect.

Conclusion

Surfactant-free formulating offers many advantages versus the conventional method of making emulsifier-based cosmetic and drug products. If the chemist is open to new approaches for creating truly unique and highly efficacious products, then the use of surfactant-free formulating will be another tool that assists in the development of the next generation of superior personal care and pharmaceutical products.

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