



Hydroalcoholic triglyceride emulsions investigated

Before addressing the specific hydro-alcoholic emulsions, a short review of emulsion technology is necessary.

Emulsification is a process that allows for the preparation of a metastable single phase of two insoluble materials. The preparation of cosmetically appealing emulsions is a very challenging and often frustrating undertaking. The metastable nature of the two insoluble materials is critical to understanding the nature and performance of emulsions. The metastable nature of the emulsion, and the requirement that the emulsion be cosmetically appealing, offer unique challenges to the formulator. This article will deal with the nature of the emulsion and what factors affect the emulsion.

Ken Klein, an expert on emulsions, defines an emulsion as: "A system of two (or more) immiscible materials (usually liquids) in which one material (the dispersed/internal phase) is suspended or dispersed throughout another material (the continuous/external phase) in separate droplets". After having said this, Ken points out the admonition offered by Graham Barker, which warns: "All emulsions are inherently unstable (with the exception of spontaneously forming micro emulsions). All we can do is delay the day when the instability will arrive."

Group opposites

The first requirement for making an emulsion is that it must be made up of two insoluble materials. If the two materials are soluble in each other, a solution is the result. Solutions are clear and can be prepared in any ratio of the two or more soluble liquids.

The most commonly understood insoluble phases are oil and water. It is a standard phrase used commonly in ordinary speech that two people are like oil and water, they simply do not mix. We are all familiar with the separation of oil on top of water in salad dressing. The lowest free energy of the system is with the two phases separated from each other.

Silicone is a third phase which like oil is insoluble in water, but at the same time

ABSTRACT

Emulsions are very important in preparation of a number of personal care formulations. Most emulsions contain a water phase and a water insoluble phase. Emulsions containing only these elements are difficult to make with the desired stability, functionality and aesthetics. If one adds ethanol, a material that partitions between the water and oil phase, preparing suitable emulsions becomes much more difficult. This paper deals with a multi-stepped approach to making difficult emulsions, one type being emulsions that contain oil, water and alcohol. In the first step the proper HLB is determined experimentally, and in the second structural variables within a particular HLB are investigated. This combined approach provides very stable emulsions.

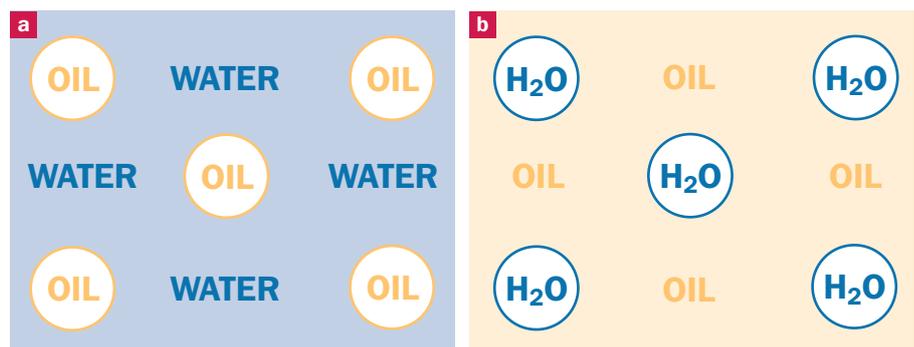


Figure 1: a) Oil-in-water emulsion, and b) Water-in-oil emulsion.

is insoluble in oil. This third phase complicates our simple system of water and oil soluble. This model is even further complicated when one considers fluoro compounds which are insoluble in other three. When one talks of oil phase, a full description of the nature of the oil needs to be provided.

Hydrophobic materials

Hydrophobic literally means water hating. By calling a materials hydrophobic, we simply define a material by what it is not (water loving) by what is. Hydrophobic materials can be soluble in silicone, oil, or fluoro phases, which are all insoluble in water and each other. To really define the material an expanded vocabulary is needed. We have proposed the list as shown in Table 1.

Why are these terms important? There are a number of very practical reasons. A key concept we need to keep in mind is the old adage that likes dissolve likes. This leads us to the understanding that the

most stable emulsions will be the ones in which there is compatibility between the different phases obtained by selecting a surfactant that has some affinity for each phase present. In today's world of personal care products water, silicone, oil and fluoro compounds are quite common.

An example of the importance of the proper selection of hydrophobic materials is seen in the carpet industry. Carpets have

Table 1: Vocabulary.

Class	Definitions
Water insoluble	Lipophilic – Oil loving
	Siliphilic – Silicone loving
	Fluorophilic – Fluoro loving
Silicone insoluble	Lipophilic – Oil loving
	Hydrophilic – Water loving
	Fluorophilic – Fluoro loving
Fluoro insoluble	Lipophilic – Oil loving
	Siliphilic – Silicone loving
	Hydrophilic – Water loving

hydrophobic agents added to make them repel water. The choice of the material used to make the carpet hydrophobic has a dramatic impact upon the usefulness of the carpet. If an oil soluble material is used to provide the coating, the carpet will have the desired water repellency that is it will be hydrophobic, but it will have an affinity for oil. Since cooking oil is quite common in homes, any spilled on the carpet so treated will be rapidly absorbed and very difficult to remove. Fortunately, most homes do not have silicone oil in them and consequently a silicone coating to provide hydrophobicity is preferred. This also explains the popularity of fluoro coatings for carpet and fabric.

This can be important in pigmented products. Almost all pigments are 'coated' today. This coating process provides products that range from simple non-bonder coatings to chemically resistant permanent bonding to the pigment. In preparing an emulsion containing a coated pigment the emulsifier should have an affinity for the coating on the pigment. Silicone coated pigments should be used with silicone emulsifiers, fluoro-coated pigments should be used with fluoro emulsifiers. However, if the coating is merely chem-absorbed on the pigment it will end up in the phase in which it has its lowest free energy and might well migrate from the pigment on storage. This can easily manifest itself in poor oven stability. The instability is caused by pigment coating, not by improper choice of emulsifiers. The nature of the coating is critical to formulation.

Emulsion terminology

The selection of the emulsifier is normally the salient characteristic that determines if an oil in water or water in oil emulsion is

Table 2: Definitions.

Dispersed phase	The phase which is disrupted or finely divided within the emulsion.
Continuous phase	The phase or medium in which the dispersed phase is suspended.
O/W (oil-in-Water) emulsion	An emulsion in which the oil phase is dispersed into a water phase, e.g. mayonnaise, whipped toppings, infant formulas, salad dressings, or lotions.
W/O (water-in-Oil) emulsion	An emulsion in which the water phase is dispersed into the oil phase, e.g. margarine, icings, or some hand creams.



Figure 2: Sheer mixer – laboratory evaluation. Result – 24-hour stability in J-208-412.

formed. Low HLB emulsifiers (i.e. those that are oil soluble) tend to give water in oil emulsions while high HLB emulsifiers give oil in water emulsions (Fig. 1).

Continuous phase

The continuous phase is the phase that is also called the external phase. While it is true in many emulsions that the continuous phase is the larger of the two phases as far as weight percentage is concerned it does not have to be the larger. The general rule is that if you can dilute an emulsion with water without

splitting it is a water continuous emulsion, or an O/W emulsion.

Discontinuous phase

The discontinuous phase is the phase that is dispersed into the continuous phase. Again it may be the predominant percentage by weight material, but does not have to be so.

Dispersion or emulsion

There has been much confusion generated in the difference between an emulsion and a dispersion. The former is metastable and

Formulation 1: Emulsifier formula.	
Material	%
Water	31.35
EtOH	31.35
Oil	31.35
Emulsifier (*see below)	5.00
Procedure: Place emulsifier or emulsifier blend into the oil phase. Mix well, noting clarity. Heat both phases to 50°C. Add water phase to oil phase and mix for 120 seconds using mixer. Note appearance.	
*1: Silube J208-212 [Lauryl PEG 8 dimethicone]	HLB 10
2: Silube J208-412 [Lauryl PEG 8 dimethicone]	HLB 7
3: Silube J208-612 [Lauryl PEG 8 dimethicone]	HLB 5
4: Silube J208-812 [Lauryl PEG 8 dimethicone]	HLB 3

Formulation 2: Emulsion stability.				
		A	B	C
Part A	Water	31.40	31.40	31.40
	Pemulen TR2	0.20	0.20	0.20
	TEA	0.10	0.10	0.10
	Ethanol	31.70	31.70	31.70
Part B	Soybean Oil	31.70	31.70	31.70
	PEG/PPG 16/16 dimethicone	4.90	0	0
	PEG/PPG 16/16 dimethicone Methyl Capped	0	4.90	0
	PEG/PPG 16/16 dimethicone (high MW)	0	0	4.90
Procedure: Disperse Pemulen TR-2 in water until it is hydrated fully, add TEA under mixing until uniform, then add ethanol, mix until homogenous, then heat up to 72–75°C. Combine Part B, mix well then heat up to 75°C. Add part B into part A slowly under mixing. Cool down the batch to room temperature under mixing. Then homogenise for 4 minutes at 20,000 rpm.				

can be diluted and remain stable, while the later is only stable in a thickened state. The high viscosity is required to keep the product from splitting. Antifoam compounds are dispersions. They stay together by virtue of their viscosity. If diluted they split into two phases, but can be made into one phase again only by adding thickener. Care must be exercised to make sure the so-called emulsion is indeed not a dispersion, since use of a dispersion will almost always result in an unstable product. High viscosity materials

may in fact fail to split at high viscosity, but are not stable upon dilution. True emulsions can be diluted to low viscosity with addition of continuous phase, while dispersions will split into two phases.

The hydroalcoholic emulsions in this paper differ in a significant way from standard emulsions. Specifically, the ethanol has solubility in both the oil and the water. This concept is called partition coefficient. Partition-coefficient is the ratio of concentrations of a compound in a mixture of two immiscible phases at

equilibrium. These coefficients are a measure of the difference in solubility of the compound in these two phases. Since the ethanol will be found in both phases and the ethanol's concentration is temperature dependent, the making of a stable emulsion is quite a challenge. The selection of an emulsifier has an additional effect when it is used in formulation, that effect is the altering of the aesthetics of the emulsion. In fact the emulsifier may be the primary driver in the feel of the emulsion. Silicone surfactants provide a less sticky feel than many traditional fatty emulsifiers, and consequently are recommended in emulsions for skin care.

Emulsifier kit

In order to evaluate different silicone emulsifiers, a kit has been prepared that have a range of HLB values. This kit allows for the ability to screen any oil or combination of oils to determine the HLB to best emulsify an oil or oil blend. The first set of experiments are conducted using all four emulsifiers, and allow the formulator not only the ability to evaluate emulsion stability, but also cosmetic aesthetics (Formulation 1).

The process in Formulation 1 is repeated with emulsifier blends (Table 3) depending upon the results of the first emulsion.

Results: 24-hour stability

J208-212 has water on the bottom of the emulsion and J208-612 and J208-812 had oil on top of the emulsion. The HLB that is needed to emulsify this formulation is around 7. Although it was the only test emulsifier to give a stable emulsion, the J208-212 stability was not acceptable for commercialisation.

Improving emulsion stability

Several emulsifiers having an HLB of around 7 were evaluated to look for secondary effects that would stabilise the emulsion (Formulation 2).

Photomicrographs

The photos of the micrographs (Fig. 3) show that the HLB is only one variable that affects the emulsion stability. The higher molecular weight polymeric silicone surfactants give smaller size micelles and a more stable elegant emulsion.

Conclusion

We recommend a multi-stepped approach in choosing emulsifiers. Firstly, use the kit approach to obtain a 'needed HLB' for an oil or combination of oils. Then look at structural variables in the same HLB for fine-tuning the emulsion.

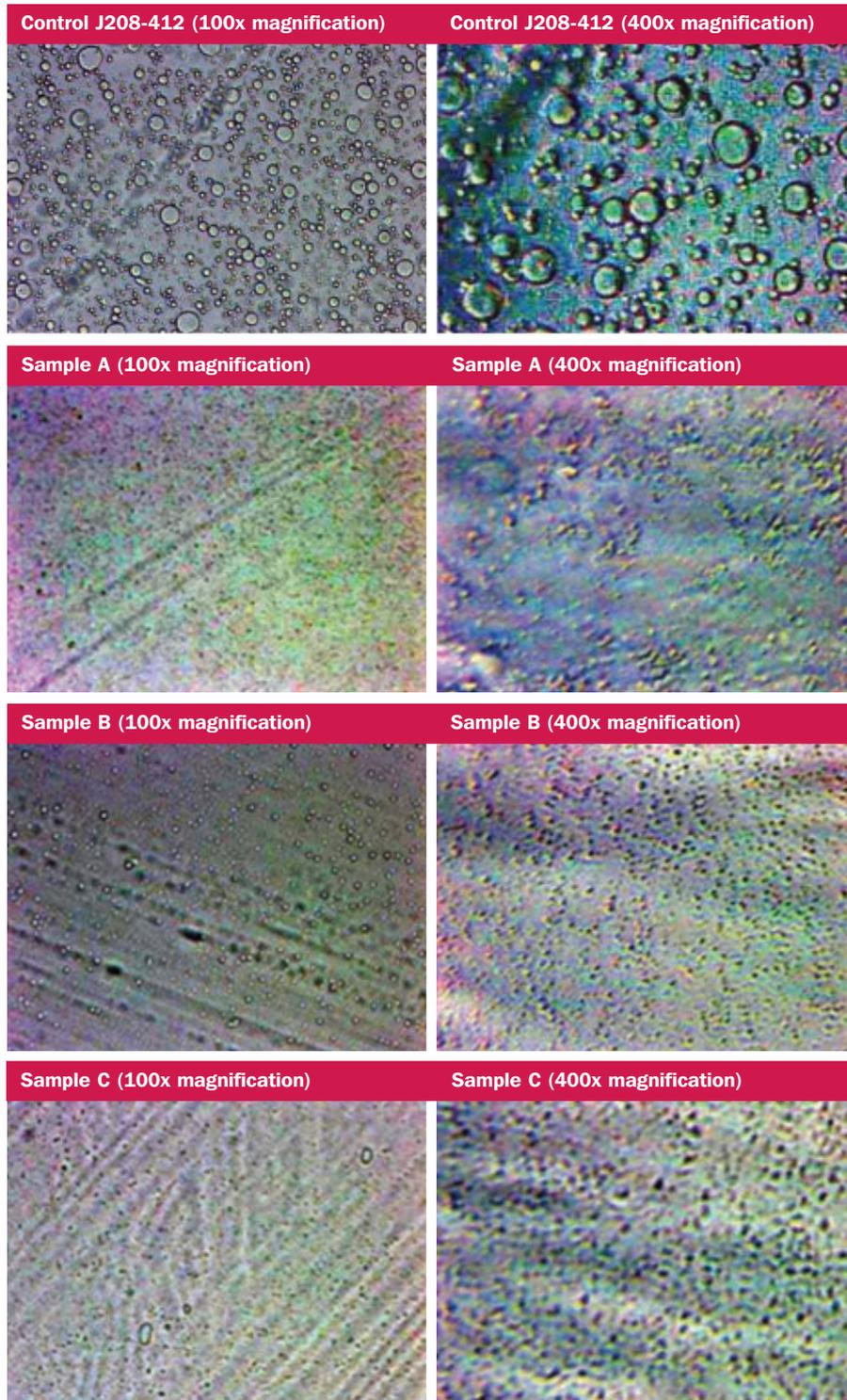


Figure 3: Photomicrographs.