



TONY O'LENICK
Siltech L.L.C., 1625 Lakes Parkway,
Suite N., Lawrenceville, GA 30043, USA

Emulsion Technology

KEYWORDS: Emulsion, Microemulsion, oil in water, water in oil, Stokes Law, HLB, Silicone emulsifier, homogenizer, alkyl dimethicone copolymer, Emulsifier test kit.

Abstract This is the fourth in the Science for Formulator series of related to silicone polymers¹⁻³. This article will deal with emulsions in general and the subsequent article will deal with the specific properties of silicone-based emulsifiers. Despite the large number of chemical classes of silicone polymers, there are several specific functional attributes that make silicone interesting in polymers used in personal care⁴. It is these functional attributes of silicone, which are a direct result of their structure that is being examined in this series of articles. As formulators, we use silicone polymers, (1) lower surface tension to levels not achievable with fatty based surfactants, (2) provide outstanding spreadability, (3) provide a highly prized aesthetic on the hair and skin and (4) are non-irritating. What is tremendously interesting in the formulation of emulsions, is not only are silicone based emulsifiers useful over the wide range of emulsion types (i.e. O/W and W/O) but recent studies indicate the emulsifier not the emollient provides 80% of the initial aesthetics to the emulsion⁴. This means that consumer acceptance comes in large part by getting the aesthetics of the emulsifier used in the formulation right.

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 Klein⁵, a pioneer in the technology of emulsions, defined 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 Barker⁶ another pioneer in the technology of emulsions, warned: "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."

Stokes Law⁷

Stokes law indicates what factors effect how rapidly an emulsion will break.

Stokes law states:

$$V=d^2(Dp)g/18h$$

wherein:

V is Velocity of sedimentation

D is diameter of particles of the dispersed phase

Dp is difference between the specific gravity of the internal and external phases

g is acceleration due to gravity

h is viscosity of the external phase

The most stable emulsions have a very slow "V" value. To make the most stable emulsion get V to approach 0.

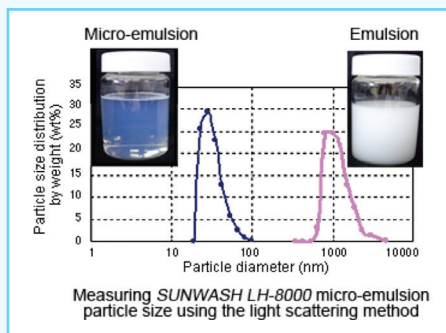
Microemulsions have a V of close to 0 and consequently are very stable.

Stokes law explains why:

1. large particle size emulsions make less stable the emulsion (d in the numerator);
2. emulsions made with internal and external phases having larger the difference in specific gravity make less stable the emulsion (Dp in the numerator);
3. emulsions are more stable on the moon than on earth, and centrifugation will cause an emulsion to split more rapidly (g is in the numerator);
4. thickening the external phase will stabilize the emulsion (h in the denominator).

Particle size in part determined by the emulsifier choice,

concentration and to which phase it is added in during the processing. Microemulsions are stable emulsions having a very small particle size (Table 1).

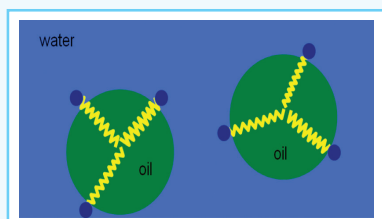


Insoluble Phases

The first requirement for making an emulsion is that it must be made up of at least two insoluble materials. This is due to the observation that if the two materials are

soluble in each other, a solution is the result. Solutions are clear and can be prepared using 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. This is due in part to the hydrogen bonding that is seen between water molecules and the fact that it takes energy to disrupt this organization with oil molecules.

Emulsifiers use their hydrophilic head and hydrophobic tail properties to prevent oily liquids separating out from the aqueous liquids (water) in which they are suspended. Table 2 shows the so-called surfactant emulsification model.



Hydrophobic Materials (Oil Phases)

Hydrophobic literally means water hating. By calling a material hydrophobic, we simply define a material by what it is not (water loving) not by what is.

By simply defining water insoluble materials as hydrophobic ignores the fact that there are a wide range of compounds that have a range of polarity and consequently all hydrophobic materials cannot be treated the same in making emulsions. Why are these terms important? The required HLB to emulsify the oils are different. Polar oils generally have a required HLB of around 5, while nonpolar oils are around 3, with isohexadecane around 2. Expecting to make stable emulsions, without testing the emulsifier is foolhardy. Time spent in the laboratory evaluating the "HLB" will pay dividends in producing the most efficient emulsion systems.

Hydrogen Bonding and Free Energy

Chemists all recall from physical chemistry that systems left alone will tend to the lowest free energy or most random state. The laws of thermodynamics win out with time, which is why we define emulsions as metastable. Even the best products given enough time will break and revert to the lowest free energy. The trick for the emulsion chemist is to minimize the difference between the emulsion's free energy and the lowest free energy and to maximize the time it takes for the emulsion to break.

Class	Definitions
Water insoluble	Extremely non-polar (isohexadecane) Non polar (Hydrocarbons) Slightly polar (High molecular weight esters) Polar (Triglycerides)

We could at first glance consider oil floating on water as a more ordered state than if oil is in the water. This observation is an indication of the important often overlooked property of water, namely hydrogen bonding. Water is very different from many other compounds. It has a very high boiling point when one considers its molecular weight (100°C for water with a molecular weight of 18, and 30°C for methanol with a molecular weight of 32. Water also has a very high surface tension, 76 dyne/cm². Water unlike most other compounds increases in volume as it freezes. We are all familiar with the broken bottle of water that occurs when we put a full bottle of room temperature water in the freezer. These properties are all related to the ability of water to form intermolecular hydrogen bonds. In fact, life as we know it requires water related to these unique properties.

Anything that disrupts hydrogen bonding will require a lot of energy. In order to get even a temporary uniform mixture of oil and water, a vigorous shake or agitation is required. This energy is used to break up hydrogen bonding. Stable emulsions are those that minimize the disruption of hydrogen bonding. As should become clear this can be achieved in several ways.

EMULSION TYPES

Traditional Non-ionic Surfactants

The selection of a surface-active agent for a specific emulsification application has been made simpler and more systematic by the development of the HLB System. The system proposed by Griffin some 50 years ago and widely promoted by ICI, is a very valuable aide to the formulator.

HLB SYSTEM¹⁰

HLB, the so-called Hydrophile - Lipophile Balance, is the ratio of oil soluble and water-soluble portions of a molecule. The system was originally developed for ethoxylated products. Listed in Table 1 are some approximations for the HLB value for surfactants as a function of their solubility in water. Values are assigned based upon that table to form a one-dimensional scale, ranging from 0 to 20.

We are using the generic term "hydrocarbon" to designate the oil soluble portion of the molecule. This generic term includes the more specific terms fatty, lipid, and alkyl.

Solubility in Water	HLB Value	Description
Insoluble	4 - 5	water in oil emulsifier
Poorly dispersible (milky appearance)	6 - 9	wetting agent
Translucent to clear	10 - 12	detergent
Very soluble	13 - 18	oil in water Emulsifier

There are two basic types of emulsions envisioned by the current HLB system. They are the oil in water (O/W) and the water in oil (W/O). The phase listed first is the discontinuous phase. That is it is the phase that is emulsified into the other. Bancroft³ postulated that upon mixing of the two phases with a surfactant present, the emulsifier forms a third phase as a film at the interface between the two phases being mixed together. He also predicted that the phase in which the emulsifier is most soluble will become the continuous phase. The continuous phase need not be the predominant quantity of material present. There are emulsions where the discontinuous phase makes up a greater weight percent than the continuous phase. A simple test is if the emulsion is readily diluted with water, water is the continuous phase.

The HLB system has made it possible to organize a great deal of rather messy information and to plan fairly efficient systematic approaches to optimize emulsion preparation. If one pursues the concept too far however the system tends to lose itself to complexities. HLB makes a great start in evaluating emulsions, but there are many other factors to consider.

CALCULATION OF HLB

The HLB system, in its most basic form, allows for the calculation of HLB using the following formulation:

$$HLB = \frac{\% \text{ Hydrophile by weight of molecule}}{5}$$

Example Oleyl alcohol 5 E.O.

$$\frac{M.W. \text{ Hydrophile (5) (44) = 220}}{\text{Total M.W of molecule}} = 45.0 \%$$

HLB= 45% / 5 = 9.0 HLB = 9.0

APPLICATION OF HLB

One can predict the approximate HLB needed to emulsify a given material and make more intelligent estimates of which surfactant or combinations of surfactants are appropriate to a given application. When blends are used the HLB can be estimated by using a weighted average of the surfactants used in the blend.

It must be clearly understood that there is no replacement for laboratory experimentation to make the emulsions that these tools predict. This is of particular interest if the oil phase has more than one component present. Since almost all formulations contain a blend of oily materials, laboratory testing is critical.

For those materials that are not listed above, it is recommended that the oil be tested using specific blends of known emulsifiers. This allows the formulator to calculate the HLB needed to emulsify the non-listed oil. The appearance of the emulsion is dependant upon the particle size of the discontinuous phase.

HLB NEEDED TO EMULSIFY			
Acetophenone	14	Lanolin	12
Acid, Lauric	16	Lauryl amine	12
Acid, Oleic	17	Mineral spirits	10
Beeswax	9	Nonylphenol	14
Benzene	15	Orthodichlorobenzene	13
Butyl Stearate	11	Pine oil	16
Carbon Tetrachloride	16	Toluene	15
Castor oil	14	Xylene	14
Chlorobenzene	13	Kerosene	14
Cottonseed oil	6	Cyclohexane	15
Petrolatum	7	Chloronated paraffin	8

Particle size
(in nanometer)

Size	Appearance
> 1	White
0.1 -1.0	Blue White
0.05 - 0.1	Translucent
< 0.05	Transparent

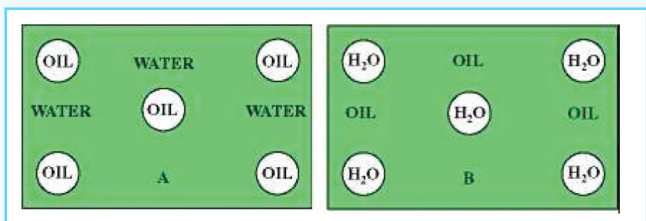
Formulation Tip

All systems that are based upon structural characteristics need to be understood as first approximations for determination of the proper emulsifier. There simply is no substitute for laboratory preparation and human evaluation when it comes to picking emulsions that have the best aesthetics and stability.

Emulsion Terminology

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

The graphic, below illustrates the O/W (A) and W/O (B) emulsions:



I. 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, the emulsion is water continuous, that is an O/W emulsion.

II. 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.

III. Dispersion or Emulsion

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

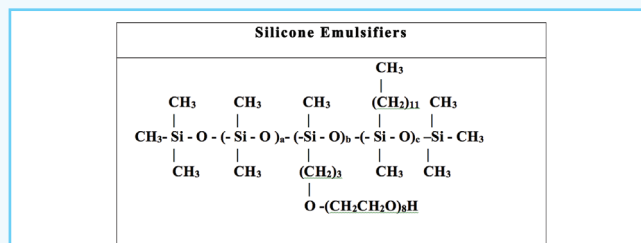
One must understand that the production of stable emulsions requires two aspects; (1) a compositional aspect, and (2) a process aspect. Not only is the selection of oil phases and the selection of the emulsifier critical to the creation of a stable aesthetically appealing emulsion, but the processing is a likewise critical.

Selection of Silicone Emulsifiers

Silicone emulsifiers are not one product but a mixture of related polymers called oligomers. A major problem with these products can be phase separation, most commonly in cold weather. This is due to the fact that when the number of each type of group in the emulsifier is low, there are molecules that lack those groups entirely. This means that you can have a mixture of molecules some containing zero water-soluble groups, and others with zero alkyl portion in the same mixture. If this product gets cold phase separation will occur. Separation will cause tremendous difficulty in production especially if you are using part drums of emulsifier, where the entire drum may not be homogeneous from top to bottom. Depending upon which phase or phases actually get into a batch, the HLB of the emulsifier can vary widely, resulting in unstable and unpredictable emulsions. The silicone emulsifier must be homogeneous and stable to low temperature. In order to select the proper emulsifier for a particular application, there need to be a number of different "3D HLB" materials that have roughly the same molecular structure.

One such series of products assembled to make emulsions have the INCI name Lauryl PEG-8 Dimethicone¹¹. The difference among them is the percentage alkyl, silicone and PEG. These differences make surfactants with different 3D HLB values.

The structure of the compounds is shown below:



Emulsifier Composition

The emulsifiers ranging in HLB from 3.2 to 9.6. This range of emulsifiers allows for the emulsification of a wide range of oils.

Product	% PEG	% Alkyl	HLB
J208-212	48	6	9.6
J208-412	39	13	7.8
J208-612	28	22	5.6
J208-812	16	32	3.2

A kit of emulsifiers shown above is available and it takes some of the stress out of formulating. These molecules are

composed of three parts; (1) an alkyl soluble part; (2) a water-soluble part and (3) a silicone soluble part. Choosing the right ratio of the three parts is critical in creating a stable emulsion. As the required HLB of your formulation changes with selection of oil or oils, the HLB of your emulsifier will change along with it.

Emulsion Formulation

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. The formulation is shown;

Emulsifier Formula

Material	%
Water	47.25
Oil	47.25
Emulsifier	5.00
Salt	0.5

Procedure:

1. Place emulsifier or emulsifier blend into the oil phase.
2. Mix well, noting clarity.
3. Add salt to water phase.
4. Heat both phases to 50°C

5. Add water phase to oil phase and using mixer mix for 120 seconds.
6. Note appearance.

The above process is repeated with emulsifier blends depending upon the results of the first emulsion



Sheer Mixer – Laboratory Evaluation

Product Evaluation

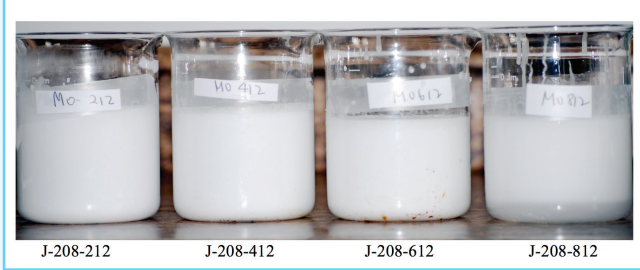
Typical results are shown below. Two of the formulations are emulsions, and the others are not. This

means the HLB needed for the emulsion is between that of Silube -208-212 and Silube J208-412.

The process is repeated using blends of Silube J208-212 and Silube J208-412 until optimized. The material is then homogenized using commercial equipment.

Mineral Oil

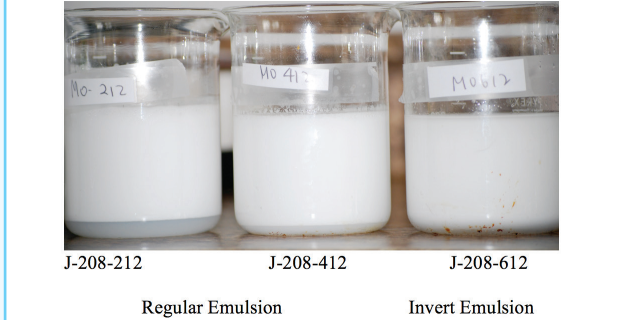
Time = 0



Time = 3 hours

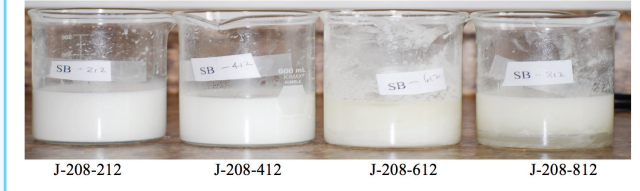


Time = 24 Hours

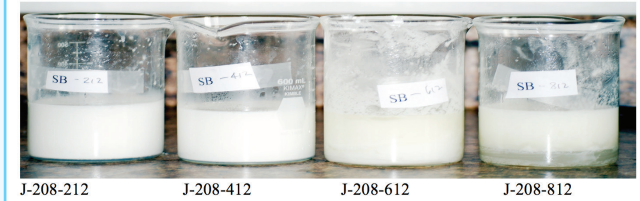


Soybean oil

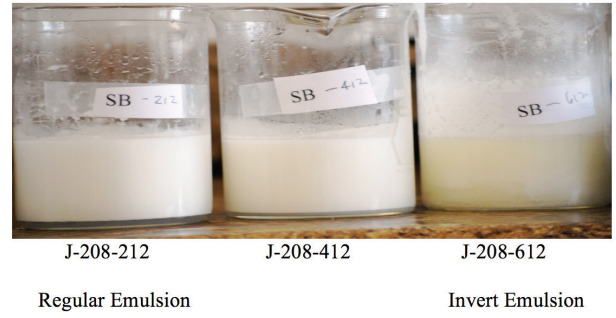
Time = 0



Time = 3 hours



Time = 24 hours



Other Considerations

Dr. Lin, an expert in emulsion technology has stated "The ability of the oil phase (with oil phase emulsifiers) to solubilize water is inversely proportional to the final particle size of the emulsion"¹²

In his pioneering work Dr. Lin teaches a process in which the oil phase to which has been added emulsifier is heated to emulsification temperature and stirred. Water is slowly added until a cloudy oil phase is seen.

Dr. Lin's article states "In the course of investigating the effects of SURFACTANT LOCATION on O/W EMULSIFICATION, it was discovered that there existed a useful correlation between the maximum amount of aqueous phase that could be solubilized in the oil phase containing the emulsifier and the average droplet size of the emulsion subsequently formed."

This method can be used to

- i. Choose emulsifiers
- ii. Determine optimal concentration of emulsifiers
- iii. Determine effects of "oil" components on emulsion stability

Processing – The under appreciated Step Homogenizer

Homogenization is a mechanical treatment to lower particle size of the discontinuous phase brought about by passing the emulsion under high pressure through a tiny orifice, which results in a decrease in the average diameter and an increase in number and surface area, of the oil globules. The net result, from a practical view, is a much reduced tendency for separation. Three factors contribute to this enhanced stability: a decrease in the mean diameter of the globules (a factor in Stokes Law), a decrease in the size distribution of the globules (causing the speed of rise to be similar for the majority of globules such that they don't tend to cluster during creaming), and an increase in density of the globules (bringing them closer to the continuous phase).

Auguste Gaulin's patent in 1899 consisted of a 3 piston pump in which product was forced through one or more hair like tubes under pressure. It was discovered that the size of fat globules produced were 500 to 600 times smaller than tubes. The homogenizer consists of a 3 cylinder positive piston pump (operates similar to car engine) and homogenizing valve. The pump is turned by electric motor through connecting rods and crankshaft.

Colloid Mill

A colloid mill does its work by hydraulic shear, bringing to

bear a tremendous amount of energy on a small portion of material in the form of a thin film. This action overcomes the strong polar forces which bind together small clumps of solids or which hold together drops of liquid. A colloid mill will not break down hard crystalline particles by fracturing them across the crystal planes as an impact type mill would do. It will, however, reduce these particles down to their ultimate crystal size by breaking up the agglomerates into which they form.

In the case of emulsions, the same principle holds. As the particles of the dispersed phase of the emulsion get smaller and smaller it requires progressively more energy to overcome the surface tension holding them together. Enormous hydraulic shear is needed to do the job and a colloid mill is an ideal means of accomplishing it.

Emulsion Stability

The following factors contribute to improved emulsion stability:

1. *Interfacial Tension* - As indicated above, most emulsifying agents are amphiphilic compounds. They will concentrate at the oil-water interface, producing a significant reduction of the interfacial tension and will need less energy to form emulsions. Despite a lowering of interfacial tension when surface-active agents are added, the free energy of the interface remains positive, leaving a persisting state of thermodynamic instability.

2. *Repulsion by Electric Charge* - Emulsion stability is often explained by the presence of repulsive electrical charges on the surfaces of emulsion droplets. According to the DLVO theory, the dispersed particles are subject to two independent forces: the van der Waals force of attraction and the electrostatic force of repulsion arising from the presence of electrical double-layers at the particle surfaces. The net interaction between the particles is obtained by summing these two terms. If the repulsion potential exceeds the attraction potential, an energy barrier opposing collision results. If the magnitude of this energy barrier exceeds the kinetic energy of the particles, the suspension is stable. The van der Waals negative potential becomes significant only when the distance between the particles is quite small.

At intermediate distances, the repulsive potential is larger than the attractive potential. Attention should be taken on application of the DLVO theory, which was originally developed for inorganic sols (in which the dispersed phase consists of submicroscopic spherical solid particles), to emulsions (where the dispersed phase consists of oil droplets stabilized by adsorbed emulsifying agents). For example, in emulsions, coalescence involves disruption of an adsorbed film around the droplets, and calculations of the potential energy barrier opposing the collision of oil globules must take into account such factors as the distortion or flattening of the oil droplets upon close approach. However, the DLVO theory still provides a good approximation of the electrostatic contribution to emulsion stability.

Ionic surfactants contribute significantly to the stability of O/W emulsions by contributing to the establishment of electric double layers in the aqueous phase adjacent to each oil droplet. Reversibly, this mechanism is of little importance in the stabilization of W/O emulsions, since the oil phase does not generally supply counter ions in sufficient amounts to establish a strong potential gradient.

3. *Stabilization by Finely Divided Solids* - Solid particles of very small size, as compared with the size of the dispersed oil droplet, can stabilize an emulsion by adsorbing at the interface to form a physical barrier around the droplets. In addition, energy is required to dislodge solid particles from the interface, since the oil/water interface must be increased to do so. Powdered silica, various clays, basic salts and plant cell fragments are examples of such agents. The emulsion type produced and its stability depend largely on the relative abilities of the two phases to wet the solid particles. The phase that preferentially wets the solid particle tends to become the continuous phase. If the interfacial tension between solid and oil (g_{SO}) is greater than that between solid and water (g_{SW}), the contact angle (q) of the solid with the aqueous phase is less than 90° , and the major portion of the solid particle resides in the water phase, thus favoring an O/W emulsion. The converse takes place if $g_{SW} > g_{SO}$. Nevertheless, if solid particles remain exclusively in either phase, they have no stabilizing effect. On the other hand, the most stable emulsion is formed when the angle of contact between the two liquids and the solid surface is close to 90° . The surface of the solid and its contact angle may be modified by adjusting pH and by adsorbing various amphiphilic compounds to its surface. Concentration and chain length of the amphiphile's hydrophobic group are important in this regard. Based on these considerations, it has been recommended that, for the preparation of emulsions stabilized by solid particles, a surface-active substance should be added that is soluble in the least-wetting (discontinuous) phase, and that the concentration of the surface-active agent should be adjusted to give a contact angle in the vicinity of 90° between the powder and the two liquids.

CONCLUSION

The preparation of high quality emulsions includes aspects that are a science (selection of the emulsifiers) and an art (selecting processes that provide small particles). The process requires repeated testing and re-testing to optimize. While there are a number of tools that can be used to make this process easier, none replace the laboratory evaluations needed to be successful.

REFERENCES

1. 1st Article
2. 2nd Article
3. 3rd Article
4. Wichers, Johann, Taelman Marie-Claire, Wortel, Vincent, Verboom, Cock, Dedren, Chris, IFSCC Magazine Vol. 5 No. 2 2002.
5. <http://www.zenitech.com/documents/emulsions.pdf>
6. <http://www.zenitech.com/documents/emulsions.pdf>
7. https://en.wikipedia.org/wiki/Stokes%27_law
8. https://www.lion-specialty-chem.co.jp/en/technology/t02/t02_02.htm
9. <http://www.educationscotland.gov.uk/highersciences/chemistry/natureschemistry/soapsandemulsions/emulsions.asp>
10. http://www.scientificspectator.com/documents/personal%20care%20spectator/HLB_Basics.pdf
11. U.S. Patent 7,279,503 Issued October 9, 2007.
12. T. J. Lin J Soc. Cosmetic Chem. 28 457-479 August 1977 Presented at 9th IFSCC June 1976.