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Formulators Forum by Ken Klein

## **Choosing Emulsifiers**

Choosing emulsifiers is one of a formulator's most daunting tasks. How is it done?

The letters HLB (**H**ydrophilic **L**ipophilic **B**alance) most likely popped into every one of your minds.

Watch them as they float in space in front of you. This old but tried and true system is all we ever hear about. Isn't there anything else? Haven't we come up with anything better in the almost 40 years since W. Griffin (1949 Atlas Powder Company Brochure) first developed the HLB method for choosing and categorizing emulsifiers?

The answer is YES, we have- I'm here to tell you about it.

**Emulsion definitions:** What are emulsions and why are they at least somewhat stable? We can begin to answer those questions by asking another question: why does oil separate from water? An easy, but not really correct, answer is that water and oil like themselves more than they like each other due to polarity differences. Water is much more polar than oil, thus, they don't mix.

A more correct explanation, according to Dr. Robert Lohead (Society of Cosmetic Chemists lecture Newark, NJ 1998), is that water likes itself so much that it squeezes out the oil. The oil doesn't care where it is, but the water just won't let it alone and boots it out! Water is not a very nice host to oil, is it?

One can describe an emulsion, forgetting for the moment about liquid crystals, as a system where one phase (the internal phase) is dispersed as droplets in another phase (the external or continuous phase). The interfacial tension between the internal and external phases must be lowered to allow for the formation of droplets. This is called an oil-in-water (o/w) emulsion. To create this emulsion, we add emulsifiers/surfactants. These surfactants (SURFace ACTIVE AgeNTS) have a hydrophobic (literally water hating) tail that can partition (line up) into the oil (droplet) phase while their hydrophilic (literally water loving) heads line up into the water phase. Their tail should be at least 14 carbons long for them to be considered "good" emulsifiers, as opposed to surfactants only. Thus, all emulsifiers can be considered to be surfactants, but not all surfactants are emulsifiers (in the cosmetic sense of the word).

## **PIT**

One of the best methods available for choosing emulsifiers is the **Phase Inversion**

**Temperature (PIT)** system developed by Dr. Shinoda (Shinoda, K. and Kuneida, H., Phase Properties of emulsions: PIT and HLB. Encyclopedia of Emulsion

Technology, Becher, P. editor, M. Dekker, New York, 1983)) Before we can discuss how this system works or how to apply it, we must first understand ethoxylated emulsifiers and their properties.

Let's begin with a simple question:

Why are ethoxylated fatty materials soluble in water? The answer is hydrogen bonding between the epoxide (as it was once) oxygen of ethylene oxide and the hydrogen of water. Many have observed the reverse cloud point seen with ethoxylated materials. It is well known that as temperature is increased, ethoxylated surfactants become less water-soluble. This somewhat surprising observation is easily explained by considering that, as the temperature increases, the molecules exhibit more movement/vibration, Thus, hydrogen bonding is inhibited, the ethoxylate loses its water solubility, and cloudiness results.

Now, back to emulsifiers and PIT. Let's take a typical emulsion (o/w) based on ethoxylated emulsifiers. We heat each phase to 75C and add the oil phase to the water phase. The temperature is still 75°C, and the hydrogen bonding is nowhere to be found. Thus, emulsifiers that normally, at room temperature, have an HLB of 12 now have an HLB of 5. They want to form a water-in-oil (w/o) emulsion and, in fact, do. As the emulsion cools, the hydrogen bonding and the HLB of the emulsifier increases. There is a temperature, the PIT, at which the emulsion now from w/o to o/w, When this happens, the particle size decreases and the distribution of particles narrows. Both conditions make for a good emulsion. If the PIT is at least 20C above the typical storage temperature (25C), then we can be quite confident that the emulsion will exhibit excellent stability.

#### ***Determining PIT***

PIT can be determined in several ways, including observation with the naked eye. Above the PIT, the emulsion is thin, watery and generally ugly. Below the PIT, it is white, opaque, glossy and thickened. Above the PIT, the pH is unstable, while below the PIT, the pH is quite stable. Keep in mind that, above the PIT, we are trying to measure the pH of an oil phase, which, of course, is silly! Since, in order to measure a pH, you must have ionic strength and conductivity: oils have neither. In a like manner, we can monitor the PIT by measuring the actual conductivity.

**Using PIT:** Suppose your emulsion has a PIT of 40°C (a bit low), and you would like to raise it to at least 50C. You can alter the ratio, or the concentration; even change emulsifiers and emollients to see the effect on the PIT and, thus, the particle size and final stability! This system is particularly useful because it takes into account the entire emulsion and not just the oil phase components, as does the HLB system. A drawback of the PIT system is that it does not work for w/o emulsions. The emulsifiers used will continue to orient towards forming w/o emulsions (low HLB) at increased temperatures. Formula 1 is an example of a sunscreen moisturizer that will exhibit a clear PIT. Try making it, and vary the emulsifier concentration to see how it affects the PIT. If you cut the concentration in half, and the PIT does not significantly drop, you just saved some money while

reducing the irritation potential. You can also substitute an anionic emulsifier for one of the nonionics and watch the PIT dramatically raise.

### Formula I

#### Sunscreen Moisturizer SPF 8

Phase	Ingredient	%
A	Water (aqua)	71.20
A	Glycerin 96%	3.00
A	Carbomer 940	0.20
A	Tetrasodium EDTA	0.20
A	Xanthan gum	0.10
B	PEG-40-Stearate	2.50
B	Octyl p-methoxycinnamate	5.00
B	Oxybenzone	2.00
B	Glyceryl stearate (and) PEG-100 stearate	4.00
B	Dimethicone (100cs)	1.00
B	Cetearyl alcohol	0.20
B	Octyl palmitate	5.00
B	C12-15 alkyl benzoate	5.00
C	Triethanolamine 99%	0.20
E	Quaternium-15	0.15
	Total	100.00

**Procedure:** Heat A to 75°C. Heat B to 75°C. Add B to A. Add C. Cool to 40°C and add D and E. Package.

## What's Wrong with this Formula?

There are at least 15 errors in this formula for you to find, Strawberry hair conditioner lotion (clear) with holding power and sunscreen

Phase	Ingredient	%
A	Water (aqua)	61.75
A	Sodium lauryl-2 sulfate (28% active)	5.00
B	Behenyltrimonium chloride	2.00
B	Sodium stearate	1.50
B	Glycol stearate	12.00

B	PVP K90	7.50
B	Hexylene glycol	2.00
C	Phenylbenzimidazole sulfonic acid	5.00
D	FD&C Yellow#5 (0. 1% soln in mineral oil)	0.25
E	Quaternium-15	1.00
F	Lime fragrance (parfum)	2.00
G	Citric acid (qs to pH 4.0)	qs
	Total	100.00

**Procedure:** Heat A to 70°C. Add B. Cool batch to 25°C and add C,D,E, F and G.

**Errors:**

1. Sodium Lauryl Sulfate is anionic and thus does not belong in this cationic system.
2. Sodium stearate is anionic and should not be present.
3. Glycol stearate will make this "clear" system opaque. Additionally, it is never used above 3%.
4. PVP K90 level is much too high.
5. PVP K90 is very water-soluble and will not provide any hold.
6. PVP is anionic and will not be compatible in this system.
7. Phenylbenzimidazole sulfonic acid, is a water soluble sunscreen and has no place in this formula. Additionally, it must be neutralized to become water-soluble. Lastly, the use level of 5% is very high.
8. Phenylbenzimidazole sulfonic acid is insoluble at pH's below 7.0.
9. Quaternium -15 should be used at 0.1-0.2%.
10. Hexylene glycol should not be present.
11. Yellow #5 is not soluble in mineral oil.
12. A strawberry conditioner should not be yellow.
13. A strawberry conditioner should not have a lime fragrance.
14. A fragrance level of 2% is quite high. More typical would be 0.2-0.5%.
15. A cationic polymer is needed to provide holding.