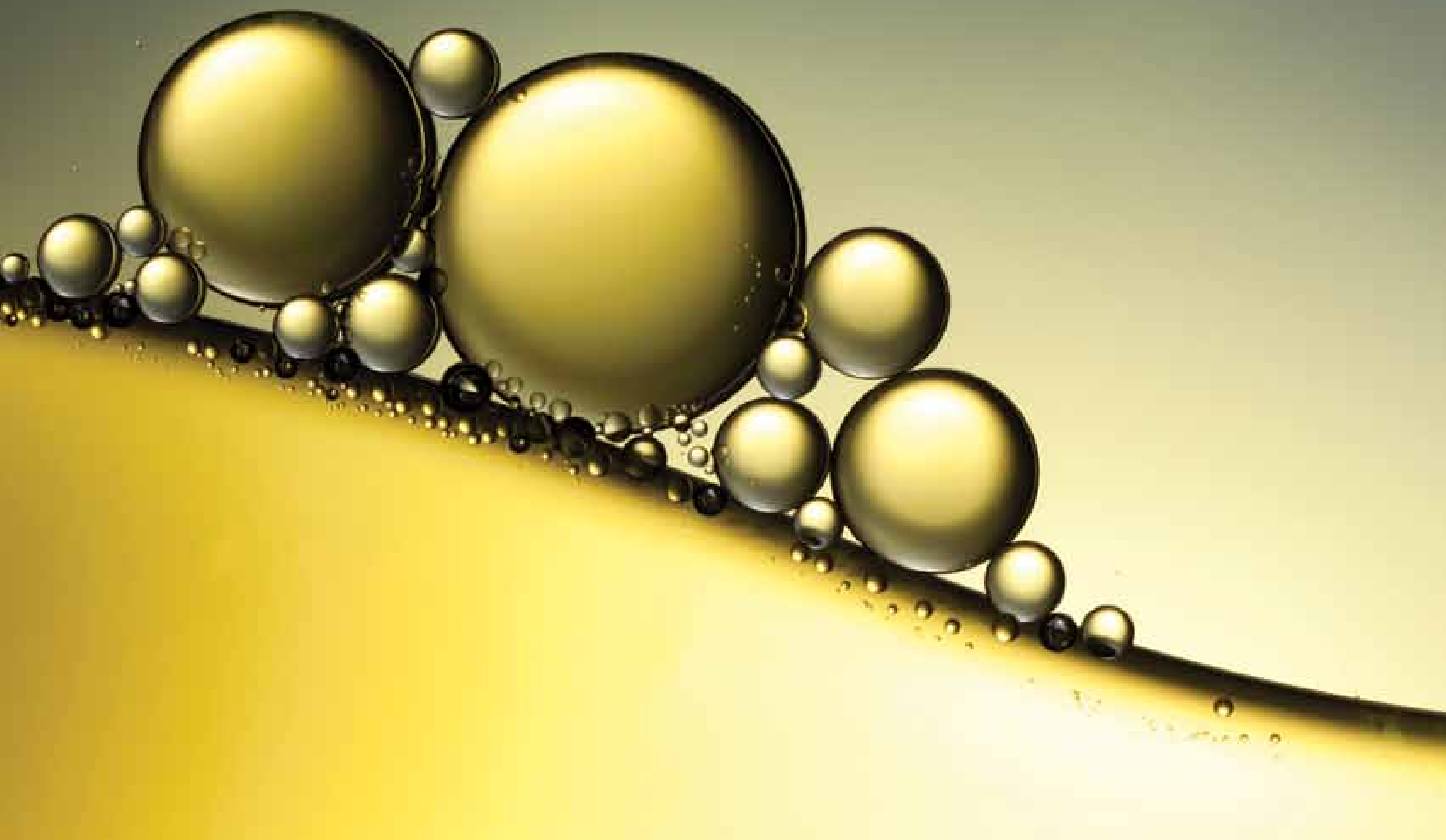
THE HLB SYSTEM

Croda's Time-Saving Guide to Surfactant Selection

Personal Care Edition



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CRODA

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Prologue

Choosing an emulsifier for your special product has never been easy; spoken from experience. It is a bit like dialing most any firm nowadays and you hear that engaging, pre-recorded voice directing you to what seems like an endless number of choices. And after you go through the first round, there is a second and even a third set of choices. For you, a formulator faced with many choices, the HLB System is a logical guide to surfactant selection. Of course, you must forgive my prejudice having used it sixty-some years ago.

A tale so familiar and yet so strange. This was my reaction when first reading The HLB System: Croda's Time-Saving Guide to Emulsifier Selection. But isn't this to be expected when one encounters a personally familiar subject that has been rewritten decades later? Languages change just like accents but so long as the story remains the same all is well.

Some of you may not be aware that the HLB System is a bit over the age of sixty. Those of you in the know will protest that the first publication was in 1949, and you are correct. Yes, the first publication was in 1949 but that was after a few years of study and lab testing. Some of the challenges of the original system still exist today, as ionic surfactants still cannot be assigned a true HLB, yet, the principle and test method used can be adapted to these situations and still help you find the best combination, as you will see later in the text.

In the early years, we faced formulating challenges in a truly wide variety of fields including industrial, textile, personal products and food. We soon realized that the choice of a surfactant for a particular use was really expedited when the choice is based on HLB testing, thus saving considerable time. It is a delight to me that the concept has survived this long and apparently still saves folks time and money and gives them good end products. May you have as much pleasure and as much good luck.

– Bill Griffin

William (Bill) Griffin developed the HLB system in the 1940's when he was a chemist with Atlas Powder Company. Atlas is now a part of Croda International Plc.

Chapter 1
Formulating an Emulsion – Challenges and Advantages

When you're faced with the task of making an emulsion, you have your choice of thousands of emulsifying agents – well over a hundred just from Croda alone. Out of this overwhelming number of products, you have the unenviable task of selecting one or two that will satisfactorily emulsify your chosen ingredients. So where do you begin?

Surfactant Selection

One of the first choices a formulator should make when developing a new emulsion should be the selection of your surfactant or surfactant blend. Your surfactant, or "surface active agent", will be of great importance as this amphiphilic molecule, generally consisting of a hydrophobic tail and a hydrophilic head, reduces the interfacial tension between your oil phase and your water phase, helping them to coalesce.

Figure 1: Sketch of a surfactant

To choose your surfactant, there are two important factors to consider. The first is chemical class. There are several chemical types of surfactants available, and each will perform differently in formulation. The four main classes of surfactants, categorized by the charge on the hydrophilic head of the molecule are:

- Anionic (negative charge)
- Cationic (positive charge)
- Amphoteric (charge dependant on the pH)
- Nonionic (no charge)

Once you have chosen the chemical class, you need to choose a surfactant or surfactant blend with the correct solubility for your application. Surfactant solubility can affect product performance, so here are some general rules to keep in mind:

- High solubility – cleansing and detergency
- Medium solubility – spreading and dispersion
- Low solubility – invert (W/O) emulsions, coupling immiscible oils
- Blend – O/W emulsions

One can predict surfactant solubility by knowing its chemical class. Therefore:

Table 1

Product Class†	Water Solubility	Oils/Fats Solubility
Soaps	Medium – High	Low
Anionics	High	Low
Cationics	High	
Amphoterics	High	
Nonionics	**	

†These are general rules and may not be true for all ingredients available.
** **Predicted by HLB**

In this text, we will address HLB and how it can assist with formulation.

What is HLB?

To help save time in surfactant selection, Atlas Powder Company (purchased by ICI in 1971 and sold to Croda in 2006) introduced, in 1949, a systematic scheme for narrowing down the relatively few emulsifying surfactants suitable for any given application. This is called the HLB System, the letters HLB standing for "Hydrophile-Lipophile Balance," and this system is still pertinent today.

All surfactants, as we explained before, have an oil loving portion and a water loving portion, or they would not have surface activity. The ratio of oil loving portion to the water loving portion is its balance, which is measured by molecular weight. Therefore, each has a water loving (Hydrophilic) to oil loving (Lipophilic) ratio (Balance) or HLB.

The HLB System was created as a tool to make it easier to use nonionic surfactants, and in general, it applies to nonionic surfactants only (more on this in Chapter 8). Basically, the HLB System enables you to assign an HLB value to the surfactant and an HLB requirement to the application for that surfactant. When these are properly matched, you can quickly and easily develop your formulation.

At least, this is the principle of the system. In practice, unfortunately, the task is never simple. But the HLB System does provide a useful guide – a series of beacons to steer you through channels where virtually no other markers exist.

Why Use the HLB System?

There are many ways to try and choose the appropriate surfactant for your application. Each has its own strengths and weaknesses. You can:

- Try what has worked in the past. *But what if you are developing a new base or are new to the industry?*
- Ask a co-worker. *But what if they do not know?*
- Use your instinct. *But what if your instinct isn't working?*
- Try everything. *But how do you test thousands and thousands of options?*
- Use the HLB System.

The HLB System can be your best option as it will often save you time, which in turn will save money. It helps you to know about the chemistry and behavior of the surfactant, and this knowledge will be of great assistance in the development of your formulations.

Chapter 2
The HLB System

As previously introduced, the HLB System can provide great assistance and save time when developing a new formulation. But, what exactly is this system? It will be useful here to provide some background and history.

A Short History of the HLB System

The HLB System was developed in 1949 by William C. Griffin of the Atlas Powder Company. He developed this system as a tool to assist with finding good emulsifier performance without having to go through significant trial and error to find a match. It was developed for use with nonionic surfactants, and each surfactant has an HLB value, ranging on a scale of 0-20.

What is the HLB System?

All nonionic surfactants consist of a hydrophilic and a lipophilic group; these are what make the molecule surface active. The hydrophilic group is usually a polyhydric alcohol (an alcohol with OH's attached) or an ethylene oxide. The lipophilic group is usually a fatty acid or a fatty alcohol. The relationship (or balance) between the hydrophilic portion of the nonionic surfactant to the lipophilic portion is what is called HLB.

In the HLB System, all nonionic surfactants have an HLB value and all applications for surfactants have an HLB requirement. When the HLB value is matched to the HLB requirement in a formulation, the formulation provides good performance (ie. More stable). It's that simple.

If HLB Value = HLB Requirement → GOOD PERFORMANCE

Figure 2: The HLB System in simple terms.

HLB Values – What do they mean?

As stated before, the HLB value of a surfactant is an expression of its Hydrophile-Lipophile Balance, i.e. the balance of the size and strength of the hydrophilic (water-loving or polar) and the lipophilic (oil-loving or non-polar) groups of the surfactant. All surfactants consist of a molecule that combines both hydrophilic and lipophilic groups.

A value can be assigned to the molecule to describe this relationship, and these values can help to infer the behavior of the ingredient. For example, a surfactant that is lipophilic in character is assigned a low HLB number (below 9.0), and one that is hydrophilic is assigned a high HLB number (above 11.0). Those in the range of 9-11 are intermediate.

HLB Related to Solubility

The HLB of a surfactant is also related to its solubility. Thus, a surfactant having a low HLB will tend to be oil-soluble, and one having a high HLB will tend to be water-soluble, although two emulsifiers may have the same HLB and exhibit quite different solubility characteristics.

Anyone who works with emulsifiers soon becomes aware of the relationship between the solubility of an emulsifier and its behavior. For example, you will use a "water-soluble" emulsifier or blend to make an O/W emulsion, to solubilize oils, or to obtain detergent action. In other words, you use a "water-soluble" emulsifier when you want your final product to exhibit aqueous characteristics, i.e. to dilute readily with water. For these purposes, you would rarely use an "oil-soluble" emulsifying system. On the other hand, if you wanted to make a W/O emulsion, or couple water soluble materials into an oil, or produce some other type of non-aqueous emulsion system, you would choose an oil-soluble emulsifier.

From experience, then, you would expect that the function of emulsifiers might well be classified by HLB, and this is true. Table 2 shows some interesting general correlations.

Table 2

HLB Range	Use
4 – 6	W/O emulsifiers
7 – 9	Wetting agents*
8 – 18	O/W emulsifiers
13 – 15	Detergents
10 – 18	Solubilizers

*The HLB range for wetting agents has been established for ambient conditions. For higher temperature applications we have established the following correlations for wetting effects:

Table 3

Application Temperature (ºC)	HLB Range
25 – 50	10 – 12
50 – 75	12 – 14
75 – 95	14 – 16

These correlations are based on long experience with Croda emulsifiers, and are amazingly accurate, although certain exceptions have been found. For example, a few excellent detergents have been found in the HLB range 11-13.

HLB and its Relationship to Cleaning

As has been discussed so far, one use of HLB is to gauge the water solubility of a given surfactant. This allows a formulator to compare two surfactants and choose the one with the appropriate water or oil solubility for the desired application. In cleaning applications, high HLB surfactants are often used to emulsify oily soils. While it is possible to match the HLB of the surfactant with the required HLB of the oil, cleaners are generally formulated to be effective on a wide range of soils. Table 2 (above) addresses guidelines as to what typical HLB values are for detergents and oil solubilizers.

Chapter 3
Determining HLB Value of a Surfactant

If the HLB System is simply matching the HLB Value of a surfactant to the HLB Requirement of the application, how do you determine the HLB Value in the first place?

References

Croda, as well as many other companies in the chemical industry, calculates and publishes the HLB values of their ingredients to make it easy to formulate using the HLB System. You can usually find this information in product literature or on the company's website.

Calculating HLB Value of a Single Surfactant

If you are unable to obtain the HLB value of a surfactant from reference material, you can perform the calculations yourself. The HLB Value for most Croda nonionic surfactants is merely an indication of the percentage weight of the hydrophilic portion of the nonionic surfactant molecule. Thus, if a nonionic emulsifier were 100% hydrophilic, you would expect it to have an HLB of 100. In the HLB system, such an emulsifier (which, of course, does not exist) would be assigned an HLB value of 20, the factor 1/5th having been adopted because of the convenience of handling smaller numbers. The HLB scale runs from 0-20, with the working scale being 0.5 – 19.5 (as no surfactants exist that would be classified with an HLB value of either 0 or 20.)

With this in mind, let's take a simple example. Let's calculate the HLB, or hydrophilic portion, of Croda's surfactant BRIJ™ O20 (oleth-20) using the theoretical composition method. (BRIJ O20 is a 20 mole ethoxylate of oleyl alcohol.)

First, you must calculate the molecular weight (MW) of the ethylene oxide. (One mole of ethylene oxide has a MW of 44; BRIJ O20 contains 20 moles.) Therefore the hydrophilic portion of BRIJ O20 has a MW of 880 (20 X 44 = 880). Next, you must determine the MW of the entire molecule. So the MW of the hydrophilic portion, the ethylene oxide, is added to the MW of the other components. In this case, there is only one other component, oleyl alcohol, which has a MW of 270.

MW ethylene oxide + MW oleyl alcohol = MW BRIJ O20

880 + 270 = 1150

Next, you need to determine the percentage (or ratio) of the MW of the hydrophilic portion to the total, so in this case, you would determine what percentage of 1150 is 880? It is 76.5%.

Lastly, the HLB uses a 1/5 factor to keep the scale small and workable. 76.5/5 is 15.3.

15.3 is the HLB of BRIJ O20!

A slightly more complicated example involves Croda's surfactant TWEEN™ 20 (polyoxethylene (20) sorbitan monolaurate). In this case, the MW of the hydrophilic portion (sorbitan + 20 moles ethylene oxide) would be 164 + 880 = 1044.

The MW of TWEEN 20 in total is 164 (sorbitan) + 200 (lauric acid) + 880 (20 moles ethylene oxide) - 18 (water of esterification) = 1226. Therefore, the HLB of TWEEN 20 would be 1044/1226 x 1/5 = 17.0.

HLB values for most nonionic emulsifiers can be calculated from the theoretical composition method, as shown above, or by using analytical data. The theoretical composition method can be inaccurate, since the "chemical name" of a surfactant is often only an approximation of the actual composition. Data obtained by actually analyzing the emulsifier is usually a better basis for determining HLB values.

Now, using the theoretical method for calculating HLB, we determined that the HLB value of TWEEN 20 was 17.0. The published HLB value for TWEEN 20 is actually 16.7, which is obtained by using the more precise analytical data method. The methodology for obtaining the actual values for most polyol fatty acid esters is explained by the calculation below:

$$HLB = 20 (1 - S/A)$$

S = saponification number of the ester (1)
A = acid number of the recovered acid (2)

In the example of the TWEEN 20, the values are as follows:

S = 45.5 avg.
A = 276 (for a commercial lauric acid)

HLB of TWEEN 20 = 20 (1-45.5/276)
HLB of TWEEN 20 = 16.7

In the case of products where the hydrophilic portion consists of ethylene oxide only, for example the MYRJ series of polyoxyethylene stearates, the formula is simply:

$$HLB = E/5$$

where E = weight percent oxyethylene content (3)

Calculating HLB Value of a Blend of Surfactants

Knowing where to get the HLB value, or how to calculate one on your own, is useful information but may not be entirely practical in a formulating sense, as most formulators use a blend of surfactants in their formulations. Indeed, we recommend using a surfactant blend as it usually provides the best outcomes.

So, how do you calculate the HLB value of your surfactant blend. It is really quite simple. You will multiply the percentage of each item in your blend by its stated HLB value and add the resulting numbers together. This will give you the total HLB (or hydrophilic portion) of your blend. Let's use the example of a 50/50 blend of BRIJ S2 (steareth-2) and BRIJ S721 (steareth-21).

BRIJ S2 has an HLB value of 4.9, so 50% of this value is 2.45.
BRIJ S721 has an HLB value of 15.5, so 50% of this value is 7.75.
The total HLB value for the 50/50 combination of BRIJ 71 and BRIJ S721 is 10.2 (2.45 + 7.75)

(1) AOCS CD 3-25
(2) AOCS Cd 6-38 and AOCS Te La-64
(3) Morgan, P.W., Determination of Ethers and Esters of Ethylene Glycol, Ind. and Eng. Chem., Anal. Ed., Vol. 18, page 500, 1946

Chapter 4
Determining Required HLB

The "Required HLB" of an Ingredient

After learning how HLB values of surfactants are calculated, how do we apply this knowledge to actually create a formulation? Remember,

If HLB Value = HLB Requirement → GOOD PERFORMANCE

We now know what the HLB value is, so what is the HLB requirement? Like the HLB value of nonionic surfactants, each lipophilic ingredient used in an O/W emulsion has an individual required HLB. These required HLBs have been determined by experimentation and long experience in formulating within these materials by Croda emulsion technologists. The required HLB for an oil is the HLB value of the surfactant that will provide the lowest interfacial tension between your oil phase and your water phase. When you are at the lowest interfacial tension between these two phases, you will need the lowest amount of surfactant to achieve a stable emulsion. In simple terms, lowest interfacial tension equals lowest amount of emulsifier. Many are listed in the table on the next page (Table 5A), but here are some general rules for required HLB in O/W emulsions:

Table 4

Class	Required HLB
Vegetable oil family	5 – 7
Silicone oils; Waxes	8 – 12
Petroleum oils	9 – 11
Fatty acids; Alcohols	10 – 12
Resins	14 – 15

So, Croda has found that all oils, waxes and other materials likely to be incorporated into emulsions have individual required HLBs. Another way to think of this is the HLB value of the surfactant that provides the lowest interfacial tension between your unique oil phase and your unique water phase is your required HLB. For instance, in Table 5A on the next page, you will see that the required HLB for a fluid O/W emulsion of paraffin is 10.

This means that a surfactant, or blend of surfactants, having an HLB of 10 will make a more stable, fluid, O/W paraffin emulsion than surfactants of any other HLB value. It does not mean that every surfactant or blend having an HLB of 10 will "work" – you might have an "HLB 10" surfactant whose chemical family does not suit the emulsion you are creating. However, you can be assured that when you're working within the proper family of surfactants, you will obtain optimum results more quickly if you work in the area of HLB 10 ± 1. You'd be wasting time to try surfactant blends at HLB 8 or 13, for example, unless you are looking for a quality other than stability in your emulsion.

Do not make the mistake of assuming, from this preliminary working data, that you should immediately try all single surfactants in the catalog that have an HLB of 10 for your paraffin emulsion. Remember, you can blend surfactants to make the HLB you want, and blends usually work best.

It is important to remember that, as noted in Table 5A, this HLB of 10 is for a 10-20% paraffin wax fluid O/W emulsion made by propeller mixing. If you want an emulsion of different concentration, composition or viscosity – or made by a different method – its required HLB will likely be different. Differences in suppliers and batches of oils and waxes can also result in variations in required HLB.

Table 5A - Required HLB for O/W Emulsions of a Variety of Emulsion Ingredients (± 1)

Acetophenone	14
Acid, Dimer	14
Acid, Isostearic	15-16
Acid, Lauric	16
Acid, Linoleic	16
Acid, Oleic	17
Acid, Ricinoleic	16
Alcohol, Cetyl	15-16
Alcohol, Decyl	15
Alcohol, Hexadecyl	11-12
Alcohol, Isodecyl	14
Alcohol, Isohexadecyl	11-12
Alcohol, Lauryl	14
Alcohol, Oleyl	13-14
Alcohol, Stearyl.	15-16
Alchol, Tridecyl	14
ARLAMOL™ PS15E.	10
ARLAMOL PB14	10
ARLAMOL PC10	10
Beeswax	9
Butyl Stearate	11
Carnauba Wax	15
Castor Oil.	14
Ceresine Wax	8
CITHROL™ PGMIS	12
CITHROL GMIS 40	15
CITHROL PG32IS	10
CITHROL PG23IS	11
Cocoa Butter.	6
Corn Oil	10
Cottonseed Oil	5-6
CRODAMOL™ AB	12
CRODAMOL CAP	8
CRODAMOL GTCC	10
CRODAMOL GTIS	8
CRODAMOL IPM	10
CRODAMOL IPIS	9
CRODAMOL ISIS	11
CRODAMOL PTIS	7
CRODAMOL SFX	4
CRODAMOL STS	9
CRODAMOL SSA	9
CRODAMOL TTIS	6
CROMOLLIENT™ DP3-A	11
CROMOLLIENT ESP	13
Cyclohexane	15
Decyl Acetate	11
Diisooctyl Phthalate	13
Diisopropyl Adipate	9
Diisopropyl Benzene	15
Dimethyl Silicone	9
ESTOL™ 1517	9
ESTOL 3609	10
Ethyl Benzoate	13
Glycerol Monostearate	13
Isopropyl Myristate	11-12
Isopropyl Lanolate	14
Isopropyl Palmitate	11-12
Jojoba Oil.	6-7
Lanolin, Anhydrous	9
Lanolin, Liquid	9
LIQUIWAX™ DIADD	5
LIQUIWAX DICDD	6
LIQUIWAX DISA	4
LIQUIWAX POLY EFA	5
MEDILAN™	8
Methyl Phenyl Silicone	7
Methyl Silicone	11
Mineral Oil (light) Napthenic	11-12
Mineral Oil, Paraffinic	10
Mineral Oil (light) Paraffinic	10-11
Mineral Oil (medium) Paraffinic	9
Mineral Spirits	14
Palm Oil.	10
Paraffin Wax.	10
Petrolatum	7-8
Pine Oil	16
Polyethylene Wax	15
Polyoxypropylene 30 Cetyl Ether.	10-11
PRIPURE™ 3759	10
PRISORINE 3505	12
PRISORINE 3515	12
Rapeseed Oil	6
SENSASIL™ PCA.	10
Silicone Oil (volatile)	7-8
Soybean Oil	6
SUPER STEROL™ LIQUID	6
Tricresyl Phosphate	17

Table 5B - Required HLB for W/O Emulsions of a Variety of Emulsion Ingredients (± 1)

Gasoline	7
Kerosene	6
Mineral Oil	6

Method of Determining Above Required Values

The figures in Table 5A, which supersede similar values published by Croda in other literature, represent the Required HLB for O/W emulsions containing 20% (or less) of the material to be emulsified.

In most cases, 2.5% to 5% of several emulsifier blends was tried, blended to HLB values 2 units apart in the range from 4 to 18. The material to be emulsified, if liquid, was blended with the emulsifier at room temperature. Solids were blended with the emulsifier at 10˚C above their necessary melting point. Water was added with propeller agitation, at room temperature for liquids, or heated to 15˚ higher than room temperature for solids.

After determination of the best one or two emulsions, 4 or 5 more emulsions were prepared with emulsifier blends one HLB unit apart, bracketing the apparently best HLB range.

The Required HLB of any material is likely to vary slightly with the source of the material, the concentration desired and the method of preparation, and should be verified against your own ingredients at your own desired concentration and with your own manufacturing techniques.

Materials that are surface active, such as fatty acids, fatty alcohols, etc., when used at high concentrations, will likely require a higher HLB.

The Required HLB for making W/O emulsions of any material will be in the range of 3 to 8; for solubilization in water in the range of 10 to 18. Typical values are shown in Table 5B.

Required HLB for Ingredient Blends

Table 5A gives you some idea of the required HLB values for O/W emulsions of various oils and waxes that you are likely to encounter most frequently. From these values, you can calculate required HLB values for blends of these oils and waxes, each component contributing its share to the whole. Knowing the required HLB of an oil or oil mixture allows you to use the least amount of surfactant to achieve emulsification.

Using the HLB system to select surfactants for an O/W emulsion is simple. For example, suppose you are making an O/W emulsion. The oil phase of the product might be 30% mineral spirits, 50% cottonseed oil and 20% castor oil to be emulsified in water. The required HLB of the combination can be calculated as follows:

Table 6

Oil Phase Ingredient	Contribution of Ingredient	x	Req. HLB	Equals
Isodecyl Alcohol	30%		14	4.2
Cottonseed Oil	50%		6	3.0
Castor Oil	20%		14	2.8
Estimated Required HLB for Emulsifier System				10

Another example is a simple O/W formula. The entire formulation consists of:

Mineral Oil	8%
Caprylic/Capric Triglycerides	2%
Isopropyl Isostearate	2%
Cetyl Alcohol	4%
Emulsifiers	4%
Polyols	5%
Water Soluble Active	1%
Water	74%
Preservative	qs

When you add up the oil phase ingredients, mineral oil through cetyl alcohol, you determine that the oil phase comprises 16% of the total formulation. In order to calculate the required HLB of this oil phase, you will need to next calculate the contribution of each ingredient to the total oil phase, as shown below:

Ingredient	% of each in total/% of oil phase to total = % contribution of oil phase
Mineral oil	8/16 = 50%
Caprylic/Capric Triglycerides	2/16 = 12.5%
Isopropyl Isostearate	2/16 = 12.5%
Cetyl Alcohol	4/16 = 25%

Table 7

Oil Phase Ingredient	Contribution of Ingredient	x	Req. HLB	Equals
Mineral oil	50.0%		10.5	5.250
Caprylic/Capric Triglycerides	12.5%		5.0	0.625
Isopropyl Isostearate	12.5%		11.5	1.437
Cetyl Alcohol	25.0%		15.5	3.875
Estimated Required HLB for Emulsifier System				11.2

In this example, we know that we should select a surfactant system with an HLB value of ~11.2. A recommendation would be to use a blend of at least two surfactants as experience has shown this to work better, mixtures of a low HLB and a high HLB surfactant typically give better coverage at the interface and a blend is more often used in formulating. (More information on the importance of blending in Chapter 6.)

Experimental Determination of Required HLB

If you are so fortunate as to find all of your oil phase ingredients listed in Table 5A, it is quite easy for you to calculate the required HLB of any combination of these ingredients for a fluid emulsion. However, what if you're using other oils or waxes with unknown HLB requirement? What if you want a thick emulsion instead of a fluid? The HLB System provides a refined trial-and-error method of determining the required HLB for any combination of ingredients to meet your own requirements for viscosity and stability. Finding the required HLB for a mixture containing components with unknown HLB requirements can be an important final step in the formulation process.

This method of calculating required HLB is often useful for fluid types of emulsions, but it is not usually practical for "solid" type emulsions. In this latter type of emulsion, an excess of lipophilic (low HLB) emulsifier, such as a stearic acid soap or SPAN™ 60 (sorbitan monostearate), is generally used for thickening action. Thus the HLB of the emulsifier combination employed will be substantially lower than the HLB value needed only for emulsification or solubilization.

Chapter 5
Determining Required HLB for Your Own Ingredients – The HLB Kit

If the ingredients of your oil phase are not shown in Table 5A, then your next step is to determine the required HLB of your ingredients by an experimental procedure. The HLB System provides you with a simple method where you actually produce a series of trial emulsions of your own ingredients, using emulsifier combinations of known HLB value. The HLB value of the emulsifier system that "works best," under your own trial conditions, is the "Required HLB" for your set of ingredients.

Even if all the required HLB values of your ingredients are published in Table 5A, it is still a good idea to run this experimental determination, because oils, waxes and solvents from various sources vary in properties and emulsifying characteristics.

Making Trial Emulsions

To determine the required HLB of a lipophilic ingredient, a simple practical test involving 8 small experiments is run. The materials needed for this test are basic: an HLB kit (available from Croda), 200 grams of your oil phase, 8 small jars and time. The instructions follow below (Using the HLB Kit).

The test will involve the preparation of 8 simple emulsions: each with the same amount of oil, same amount of surfactants but with different HLB values and each with the same amount of water. After all components are added to the jars, each is mixed. Then you wait to see which emulsion is most stable, meaning the one that is least separated or the one that separates last. The HLB value of the surfactant used in the most stable emulsion is the required HLB for that particular oil phase.

Using the HLB Kit

These are the simple steps for running the required HLB determination test:

Step 1 – assemble the equipment. You will need:

- An HLB Kit
- 8 – 2 oz glass jars with lids
- 200 grams of your oil phase
- Deionized water
- Permanent marker
- Pipette
- Measuring cylinder

Step 2 – Using a permanent marker, label the glass jars: 2, 4, 6, 8, 10, 12, 14, 16, 18

Step 3 – Into the jar labeled "2", place 2 grams of the HLB kit surfactant 2. Into the jar labeled "4", place 2 grams of the HLB kit surfactant 4. And so on, until all jars contain 2 grams each of their corresponding surfactant.

Step 4 – Add 20 grams of the oil to each jar.

Step 5 – Cap the jars and vigorously mix the oil and surfactant.

Step 6 – Open each jar and add 28 grams of deionized water to each.

Step 7 – Recap tightly and shake each jar 20 times.

Step 8 – Observe the emulsions. The one that does not separate, or the one that separates last, is the winner – the required HLB!

Running a Required HLB

Using the HLB Kit is simple as the HLB kit surfactants are premixed and ready for use. But, if you do not have an HLB kit, this is not a problem. The HLB kit is comprised of a series of jars containing the following surfactant blends:

HLB 2	8% SPAN 80 / 92% SPAN 85
HLB 4	88% SPAN 80 / 12% SPAN 85
HLB 6	83% SPAN 80 / 17% TWEEN 80
HLB 8	65% SPAN 80 / 35% TWEEN 80
HLB 10	46% SPAN 80 / 54% TWEEN 80
HLB 12	28% SPAN 80 / 72 % TWEEN 80
HLB 14	9 % SPAN 80 / 91% TWEEN 80
HLB 16	60% TWEEN 20 / 40% TWEEN 80

But you do not even need to be this precise. For your preliminary tests, to determine your required HLB, select any matched pair of SPAN and TWEEN emulsifiers, i.e. SPAN 20 with TWEEN 20 or SPAN 60 with TWEEN 60. This will give you two emulsifiers of the same chemical class, one lipophilic (oil-loving), the other hydrophilic (water-loving). For example, the "20" SPAN-TWEEN emulsifiers are both laurate esters; the "40"s are palmitate esters; the "60"s are stearates; and the "80"s oleates. The SPAN emulsifiers are lipophilic; the TWEEN products hydrophilic.

This is only a trial run, so you don't care at this point whether the emulsifiers you select are perfect for your purpose or not.

As an example, let's use SPAN 60 and TWEEN 60. As a start, make up small batches of seven emulsifier combinations, ranging in HLB from straight SPAN 60 (HLB = 4.7) to a straight TWEEN 60 (HLB = 14.9), * as follows:

Sample No.	Surfactant Blend		Calculated HLB
	SPAN 60	TWEEN 60	
1	100%	–	4.7
2	87%	13%	6
3	68%	32%	8
4	48%	52%	10
5	28%	72%	12
6	6%	94%	14
7	–	100%	14.9

*While the seven test emulsifier combinations shown here will usually give you a good indication of the "Required HLB" of your oil phase, you may find it advisable to try higher HLB values. For example, by working with SPAN 20 and TWEEN 20, instead of SPAN 60 and TWEEN 60, you can work within an HLB value range of 8.6 to 16.7.

Now, follow the directions of the HLB kit, but use your samples as above and note these HLB values on your sample bottles.

With this method as well, you will probably notice fairly quickly that one or another of these emulsifier combinations will give you a better emulsion than the other six, even though not necessarily a very good one. If all the emulsions seem fairly good, with not much noticeable difference, then repeat the seven tests, using less surfactant. Conversely, if all the emulsions are poor and show no great difference, repeat tests but use higher surfactant content.

As mentioned above, you usually will be comparing your emulsions for stability – you'll be watching for separation of ingredients, perhaps in a matter of minutes, perhaps overnight, or after heating or after freeze-thaw cycles. However, it is entirely possible your criterion for a good emulsion might be clarity or viscosity, ease of preparation or ease of application. Whatever your index for judgment might be, these preliminary tests will enable you to pinpoint an approximate HLB range (± 1) for the surfactant system that will work best for you.

In this preliminary test, you may find that you get a fairly good emulsion at HLB 4.7 and another one at HLB 12.0. If something like this occurs, you'll probably find that your "low HLB" emulsion is a W/O emulsion (doesn't dilute readily with water, doesn't conduct electricity) and your "high HLB" emulsion is an O/W emulsion (easily water-dispersible, conducts electricity). Most likely, you're trying for an O/W, but that's a matter of your own choice.

Merely by this one easy set of trials, you have already narrowed yourself down to a relatively small field for further trials of emulsifiers or emulsifier blends. Next, you will be looking for the ideal chemical type, and a later chapter in this book will give you some guideposts for this. Regardless of the chemical type finally chosen for your emulsifier or blend, it will fall fairly closely within the HLB limits you have found in these preliminary tests. You'll be wasting your valuable time if you bother looking elsewhere in the HLB range for your emulsifier answer.

Chapter 6
Surfactant Choice Considerations – General Recommendations

There are several factors to consider when choosing which surfactants will perform best in a system – even beyond HLB value. The following are important to note.

Using a Blend of Surfactants

Let's assume that you have determined the "Required HLB" of your ingredients and it's 12.0. It might appear that the proper way to proceed now would be to obtain all the emulsifiers Croda supplies having an HLB of 12, or somewhere around 12, and try them.

However, if you do this, you're very likely making a serious mistake. First, you're assuming that having the right HLB is enough. However, you must also find the right chemical type having the right HLB, as discussed below. Secondly, you're missing the opportunity the HLB System gives you to tailor-make the ideal surfactant blend for your own set of ingredients and conditions. By blending two surfactants, you can arrive at the exact HLB you need, instead of trying to "make do" with a single emulsifier having an HLB that's "close but not quite right." Moreover, you can adjust your surfactant blend to suit your oil or other active ingredients, instead of having to limit or adjust your active ingredients to suit the emulsifier.

Bear in mind that the most stable emulsion systems usually consist of blends of two or more emulsifiers, one portion having lipophilic tendencies, the other hydrophilic. Only in relatively rare instances will you find a single emulsifier product to suit your requirements, even though it might have the exact HLB you need.

Importance of Chemical Type

Knowing the "Required HLB" of your ingredients narrows down your choice of emulsifiers considerably, but you're still faced with the problem of choosing the ideal chemical type of emulsifiers. At least, when you try different chemical types, you won't need to try all sorts of blends of each chemical type – just the one blend having the "Required HLB" you need.

"Right chemical type" is just as important as "right HLB." The two go hand in hand. Suppose you found that a blend of SPAN 60 and TWEEN 60 (stearates), at an HLB of 12, gave you a better emulsion than any other HLB of these two emulsifiers. That HLB of about 12 will be best for any chemical type you might try. But now you must determine whether some other SPAN-TWEEN blend at HLB 12 (say laurates, palmitates or oleates) might not be better or more efficient than the stearates. Or perhaps some chemical family blend outside the popular SPAN-TWEEN class might be even more suitable. (In any case, remember, it should have an HLB of about 12!)

If HLB = HLB Requirement → GOOD PERFORMANCE

Table 8: HLB for O/W Emulsions of a Variety of Croda Emulsifiers (±1)			
BRIJ C10 ... 13	BRIJ S2 ... 5	SPAN 80 ... 4	TWEEN 60 ... 15
BRIJ C2 ... 5	BRIJ S20 ... 15	SPAN 85NV ... 2	TWEEN 61 ... 10
BRIJ C20 ... 16	MYRJ™ S100 ... 19	SYNPERONIC™ 13/12 ... 15	TWEEN 65 ... 11
BRIJ IC20-70 ... 15	MYRJ S40 ... 17	SYNPERONIC 13/6 ... 11	TWEEN 80 ... 15
BRIJ L23 ... 17	MYRJ S8 ... 11	TWEEN 20 ... 17	TWEEN 81 ... 10
BRIJ L4 ... 10	SPAN™ 20 ... 9	TWEEN 21 ... 13	TWEEN 85 ... 11
BRIJ S10 ... 12	SPAN 40 ... 7	TWEEN 40 ... 16	
BRIJ S100 ... 19	SPAN 60 ... 5		

Other Factors

There are several other factors to consider whenever you are creating an emulsion, and these still need to be reviewed when using the HLB System to assist in formulation. Some important factors to remember are:

- Physical form
- FDA “status,” if any
- Price vs. function
- Efficiency of the surfactant

There are, of course, others to consider as well, but these are several key ones to address when creating a new emulsion.

General Recommendation

If you are creating a topical O/W emulsion, we recommend using nonionic surfactants based on stearyl alcohol or stearic acid. We find that the high molecular weight and high melting point of the C-16/18 portion provides superior anchoring in the dispersed oil droplets with blends of BRIJ S2 (steareth-2) and BRIJ S721(steareth-21) being the most useful in providing greater resistance to coalescence.

Anionic Emulsifiers

Although HLB was developed to explain the behavior of ethoxylated, non-ionic emulsifiers, all surfactants possess both hydrophillic and lipophilic character. Since most industrial formulations contain both anionic and nonionic emulsifiers, it is helpful to have a working knowledge of how the HLB concept can be extended to include anionic surfactants.

The table below lists experimentally-determined HLB values for some commonly used anionic surfactants. When these surfactants are used in combination with nonionic emulsifiers, they perform as if their HLB values were as follows:

Table 9

Anionic Emulsifier	HLB
Triethanolamine oleate	12
Sodium oleate	18
Potassium oleate	20

Note the wide range of HLB values as the neutralizing agent is varied. Knowing that HLB requirements are accurate to within one unit, the range of performance variation that is possible by varying the neutralizing agent is very important and useful information.

Chapter 7
Chemical Types, Applications and HLB Values

While the remaining steps in your surfactant selection system are still a matter of trial and error, you have already learned a great deal about what will work and what won't work as emulsifiers in your own emulsification system, simply by using your HLB kit or via a few trials of SPAN-TWEEN emulsifier combinations blended to meet your "Required HLB."

Your procedure now will be to try to even more chemical types, blended to meet your previously determined "Required HLB." Occasionally, the "Required HLB" for one chemical type may be slightly different from that for another chemical family, but at least you have a reliable guide for your trials. Thus, if your required HLB is 12, and you try another chemical family, at HLB ranges from 11 to 13, without getting equal or superior emulsifying results as compared with your previous trials, you can immediately discard this chemical family from further consideration.

Recent studies have shown stearic acid and stearyl alcohol derivatives consistently out-perform other chemical types in a variety of emulsification work. When time is limited for investigation of various chemical types of surfactants, you would do well to concentrate on blends of SPAN 60, TWEEN 60, and BRIJ S2.

You will need to draw from your formulating experience or reference materials to determine what chemical classes will work best with various applications. There are many resources available, in textbooks or on the internet, where you can cross reference applications to surfactants or to surfactant blends for that application. These are always merely suggestions, so it is recommended that you still determine the "Required HLB" for your own particular emulsion system, as shown in Chapter 4, and test the recommended surfactants and surfactant blends in your system as products will differ between manufacturing sources.

Chapter 8
Additional Considerations

Most of this text has dealt thus far with nonionic surfactants, as this is primarily what the HLB System was designed to address. The system does quite well in addressing many nonionic surfactants. Yet, there are some instances where another method of determining HLB may be necessary.

Experimental Method of Determining HLB

While the formulas given earlier in the text are satisfactory for many nonionic emulsifiers, certain other nonionic types exhibit behavior which is apparently unrelated to their composition – for example, those containing propylene oxide, butylene oxide, nitrogen and sulfur. In addition, ionic types of emulsifiers do not follow this "weight percentage" HLB basis, because, even though the hydrophilic portion of such emulsifiers is low in molecular weight, the fact that it ionizes lends extra emphasis to that portion, and therefore makes the product more hydrophilic.

Therefore, the HLB values of these special nonionics, and of all ionics, must be estimated by experimental methods, so that their HLB values are "aligned" with those of the common Croda nonionic emulsifiers. An experimentally determined HLB value for such an emulsifier will not necessarily indicate the percentage weight of its hydrophilic portion; for example, you will find experimentally that the HLB of pure sodium lauryl sulfate is about 40, which surely does not mean that it is 200% hydrophilic (!), but merely that it shows an apparent HLB of 40 when used in combination with other emulsifiers.

The experimental method of HLB determination, while not precise, briefly consists of blending the unknown emulsifier in varying ratios with an emulsifier of known HLB, and using the blend to emulsify an oil of known "Required HLB." The blend which performs best is assumed to have an HLB value approximately equal to the "Required HLB" of the oil, so that the HLB value of the unknown can be calculated. In practice, a large number of experimental emulsions must be made, from which an average HLB value for the unknown is finally calculated.

Needless to say, such a procedure can be difficult and time-consuming. However, the lack of an exact HLB number for an emulsifier is not necessarily a serious disadvantage, since a rough estimate of HLB can be made from the water-solubility of the emulsifier, and in many instances this is adequate for screening work.

Water-Solubility Method

While this method is not an infallible guide, you can approximate the HLB of many emulsifiers according to their solubility or dispersibility characteristics as shown in Table 10.

Table 10: HLB by Dispersibility

	HLB Range
No dispersibility in water	1 – 4
Poor dispersion	3 – 6
Milky dispersion after vigorous agitation	6 – 8
Stable milky dispersion	8 – 10
Translucent to clear dispersion	10 – 13
Clear solution	13+

Chapter 9
Summary

In summary, the HLB system is a numerical system that assists you in determining how oils, water and surfactants are likely to interact. In this system, all nonionic surfactants have an HLB value, which indicates the ratio of the water loving to the oil loving portion of the molecule. The higher the HLB value of a surfactant, the more hydrophilic the surfactant is, the lower the HLB value, the more lipophilic.

In addition, oils and applications have an HLB requirement. Matching the HLB value of a surfactant to the HLB requirement of an oil will create better performance in an emulsion.

If HLB Value = HLB Requirement → GOOD PERFORMANCE

This system is useful as a time saving guide to formulating if you can match your HLB requirement to your surfactants HLB value. Considerations need to be made to chemical class, as well as other surfactant choices, but this is part of the art and science of formulating. In the meantime, this system can allow you to save much needed development time.

Using the HLB Kit

These are the simple steps for running the required HLB determination test:

Step 1 – assemble the equipment. You will need:

- An HLB Kit
- 8 – 2 oz glass jars with lids
- 200 grams of your oil phase
- Deionized water
- Permanent marker
- Pipette
- Measuring cylinder

Step 2 – Using a permanent marker, label the glass jars: 2, 4, 6, 8, 10, 12, 14, 16, 18

Step 3 – Into the jar labeled "2", place 2 grams of the HLB kit surfactant 2. Into the jar labeled "4", place 2 grams of the HLB kit surfactant 4. And so on, until all jars contain 2 grams each of their corresponding surfactant.

Step 4 – Add 20 grams of the oil to each jar.

Step 5 – Cap the jars and vigorously mix the oil and surfactant.

Step 6 – Open each jar and add 28 grams of deionized water to each.

Step 7 – Recap tightly and shake each jar 20 times.

Step 8 – Observe the emulsions. The one that does not separate, or the one that separates last, is the winner – the required HLB!

Notes

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