

# CHAPTER 1

## Meaning of HLB Advantages and Limitations

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WHEN you're faced with the problem of making an emulsion, you have your choice of hundreds upon hundreds of emulsifying agents—well over a hundred just from ICI-US alone. Out of this welter of products, you have the unenviable task of selecting one or two which will *satisfactorily emulsify* your chosen ingredients. You can choose from among hundreds of manufacturers and thousands of surface active agents, according to the 1975 edition of John W. McCutcheon's "Detergents and Emulsifiers."

Your own definition of the words "*satisfactorily emulsify*," as used above, is of course the prime factor in your choice of one emulsifier instead of another.

### What the HLB System Does

To help save time in emulsifier selection, ICI-US introduced in the late 1940's a systematic scheme of centering down on the relatively few emulsifiers suitable for any given application. This is called the HLB System—the letters HLB standing for "Hydrophile-Lipophile Balance."

Briefly, the HLB System enables you to assign a number to the ingredient or combination of ingredients you want to emulsify, and then to choose an emulsifier or blend of emulsifiers having this same number.

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.

### Where the HLB System Can Help Most

Our discussion here will assume that you have had some experience in making emulsions. A complete dissertation on the many factors which influence your choice of emulsifiers would necessarily cover aspects of emulsion technology far beyond the HLB System.

For example, before you can begin making use of the HLB System, you must set up some sort of evaluation system for your "satisfactory" emulsion. Do you want an oil-in-water (O/W) emulsion or a water-in-oil (W/O)? How *stable* do you want your emulsion, in storage?—in use? What are your *cost limits*? Should your emulsifier be stable toward alkalis, salts, or electrolytes? Must it be non-toxic—or non-irritating to the skin? How about your manufacturing equipment

—or the equipment your customer might use in applying your emulsion product—will *ease of preparation or application* affect your choice of emulsifier?

Such factors as this may immediately lead you to discard certain types or groups of emulsifiers from further consideration. In any case, they will certainly influence your choice of emulsifiers when you are weighing the relative merits of one emulsion or another in final trials.

### HLB Numbers of Emulsifiers— What Do They Mean?

In the HLB System, each emulsifier is assigned a numerical value which we call its HLB. The HLB of ATLAS emulsifiers is shown in all current ATLAS emulsifier literature, and similar values may be calculated or estimated by various means for any emulsifier. Methods for determining this HLB value are discussed in Chapter 7.

The HLB of an emulsifier 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 emulsifier. All emulsifiers consist of a molecule that combines both hydrophilic and lipophilic groups.

An emulsifier 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.

When two or more emulsifiers are blended, the resulting HLB of the blend is easily calculated. For example, suppose you want to determine the HLB value of a blend comprising 70% of TWEEN 80 (HLB = 15) and 30% of SPAN 80 (HLB = 4.3). The calculation would be:

$$\begin{aligned} \text{TWEEN 80} & 70\% \times 15.0 = 10.5 \\ \text{SPAN 80} & 30\% \times 4.3 = 1.3 \\ \text{HLB of blend} & = 11.8 \end{aligned}$$

As you will discover in applying the HLB System, the HLB of an emulsifier or blend of emulsifiers is an excellent indication of *what the emulsifier system will do*, that is, whether it will make an oil-in-water (O/W) emulsion or a W/O emulsion, or act as a solubilizer for some oil. The HLB of an emulsifier class

or blend is also an indication of the efficiency of chemically-related emulsifiers or of a blended pair of emulsifiers for performing any given emulsifier task.

When you consider a variety of chemical types of emulsifier, and classify them according to structure, each class covers a segment of the HLB range. The efficiency of these classes differs. HLB is not an indication of the relative efficiency of one class to another. This "class efficiency" seems to be related more to chemical structure (that is, whether the emulsifier is a soap, a partial ester, a complete ester, whether the lipophilic group is saturated, etc.) and the relationship of its chemical structure to the chemical structure of the material to be emulsified.

Subsequent chapters in this book will give you some guides to comparison of chemical types when the "ideal" HLB of emulsifier for your application has been determined, although no specific rules have been established for this step in emulsifier selection.

#### HLB Related to Solubility

The HLB of an emulsifier is related to its *solubility*. Thus, an emulsifier 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 yet 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, or 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 functions of emulsifiers might well be classified by HLB, and this is true. Table 1 shows some interesting general correlations.

Table 1

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

These correlations are based on long experience with ATLAS 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.



When oil-loving groups in surfactant are predominant, HLB is low . . . for producing water-in-oil emulsions.

When water-loving groups predominate, the surfactant has high HLB and is used for oil-in-water emulsions.

When oil-loving and water-loving groups are fairly well balanced, HLB is intermediate (around 10).

## CHAPTER 2

### "Required HLB" for Typical Ingredients to be Emulsified

#### The "Required HLB" of an Ingredient

Through long experience in using the HLB System, ICI-US emulsion technologists have found that all oils, waxes and other materials likely to be incorporated into emulsions have an individual "Required HLB." For instance, in Table 2A, you will see that the required HLB for a fluid O/W emulsion of paraffin is 10.

This means that an emulsifier, or blend of emulsifiers, having an HLB of 10 will make a more stable fluid O/W paraffin emulsion than emulsifiers of any other HLB value. It *does not mean* that every emulsifier or blend having an HLB of 10 will "work"—you might have an "HLB 10" emulsifier of the "wrong" chemical family (wrong for this purpose, at least). However, you can be assured that when you're working with any certain family of emulsifiers, you will obtain optimum results more quickly if you work in the area of HLB 10, say  $\pm 1$ . You'd be wasting time to try emulsifier blends at HLB 8 or 13, for example, unless you might happen to be looking for a particular 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 emulsifiers in the catalog that have an HLB of 10 for your paraffin emulsion. Remember, you can *blend* emulsifiers to make any HLB you want, and blends usually work best. In Chapters 5 and 6, emulsifier blends and selection of "chemical families" for trial will be discussed more fully.

It is important to remember that, as noted in Table 2, 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 supplies and batches of oils and waxes can also result in variations in required HLB.

#### Required HLB for Ingredient Blends

Table 2 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.

For example, suppose you are making an O/W emulsion textile lubricant. The product might be 30% mineral spirits, 50% cottonseed oil and 20% chlorinated paraffin to be emulsified in water. The required HLB of the combination can be calculated as follows:

Mineral Spirits . . . . . 30%  $\times$  Req. HLB 14 = 4.2  
 Cottonseed Oil . . . . . 50%  $\times$  Req. HLB 6 = 3.0  
 Chlorinated Paraffin . . . . . 20%  $\times$  Req. HLB 8 = 1.6

Estimated HLB for emulsifier system . . . . . 8.8

You should check this estimated value with a few exploratory tests in the range of say 8-10, as shown in Chapter 3, but you know from this calculation that

Table 2A—Required HLB of Various Emulsifier Combinations

Ingredient	HLB Value	Ingredient	HLB Value
Acetophenone	12	Methyl Phenyl Ether	12
Acid, Dimethyl	13	Silica, Fumed	13
Acid, Isononyl	14	Sorbitan Monooleate	14
Acid, Lauric	15	Sorbitan Monooleate	15
Acid, Myristic	16	Sorbitan Monooleate	16
Acid, Ricinoleic	17	Sorbitan Monooleate	17
Alcohol, Cetyl	18	Sorbitan Monooleate	18
Alcohol, Dodecyl	19	Sorbitan Monooleate	19
Alcohol, Heptyl	20	Sorbitan Monooleate	20
Alcohol, Isodecyl	21	Sorbitan Monooleate	21
Alcohol, Labryl	22	Sorbitan Monooleate	22
Alcohol, Oleic	23	Sorbitan Monooleate	23
Alcohol, Stearyl	24	Sorbitan Monooleate	24
Alcohol, Tridecyl	25	Sorbitan Monooleate	25
Azonal B	26	Sorbitan Monooleate	26

Table 2B—Required HLB of Various Emulsifier Combinations

Ingredient	HLB Value	Ingredient	HLB Value
Guar Gum	13	Sorbitan Monooleate	13
Method, emulsion	14	Sorbitan Monooleate	14
The HLB of an emulsion is the sum of the HLBs of the ingredients.		Sorbitan Monooleate	
HLB of oil phase + HLB of emulsifier = HLB of emulsion.		Sorbitan Monooleate	
to emulsify 10% oil in water, you need an emulsifier with an HLB of 18.		Sorbitan Monooleate	
to emulsify 20% oil in water, you need an emulsifier with an HLB of 16.		Sorbitan Monooleate	
to emulsify 30% oil in water, you need an emulsifier with an HLB of 14.		Sorbitan Monooleate	
to emulsify 40% oil in water, you need an emulsifier with an HLB of 12.		Sorbitan Monooleate	
to emulsify 50% oil in water, you need an emulsifier with an HLB of 10.		Sorbitan Monooleate	
to emulsify 60% oil in water, you need an emulsifier with an HLB of 8.		Sorbitan Monooleate	
to emulsify 70% oil in water, you need an emulsifier with an HLB of 6.		Sorbitan Monooleate	
to emulsify 80% oil in water, you need an emulsifier with an HLB of 4.		Sorbitan Monooleate	
to emulsify 90% oil in water, you need an emulsifier with an HLB of 2.		Sorbitan Monooleate	
to emulsify 100% oil in water, you need an emulsifier with an HLB of 0.		Sorbitan Monooleate	

emulsifier combinations in this range will probably give best results.

This method of calculating required HLB is often useful for fluid types of emulsions, but is not usually practical for "solid" cream type emulsions or very heavy lotions. 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.

**Experimental Determination of Required HLB**

If you are so fortunate as to find all your oil phase ingredients listed in Table 2A, 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 of unknown "required HLB"? 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. Chapter 3 will discuss this method in detail.

# CHAPTER 3

## Determining "Required HLB" for Your Own Ingredients

If the ingredients of your oil phase are not shown in Table 2A, 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. Essentially, this method consists in actually producing 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 when all the required HLB values of your ingredients are published in Table 2A, 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**

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.

Suppose you happen to have some SPAN 60 and TWEEN 60 on your lab shelf. You can use these for your trials. 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.	Emulsifier 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

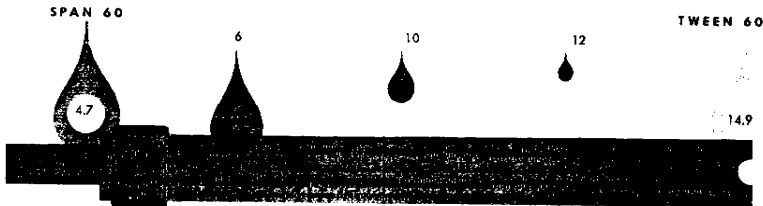
\*HLB values of all ATLAS surfactants are given in the booklet: "General Characteristics of ATLAS Surfactants" (O-1), and many representative chemical types are also listed in Chapter 6. While the seven test emulsifier combinations shown here will usually give you a good indication of the "Required HLB" 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 could try HLB values from 8.6 to 16.7.

Now, make seven test emulsions, using one of the above emulsifier samples in each. Use an excess of emulsifier (say 10-20% of the weight of your oil phase), and dissolve or intimately disperse the emulsifier into the oil phase, melting ingredients together if necessary.

While simple mixing of your ingredients and emulsifiers will probably be sufficient at this point in your testing, it is important that you use preparation methods as nearly identical as possible for each of your seven emulsions, simulating your own plant methods.

Using the appropriate method or methods for comparison and evaluation of *your products*, 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 emulsifier. Conversely, if all the emulsions are poor and show no great difference, repeat the tests but use higher emulsifier content.

More often than not, you 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 center down on an approximate



HLB range (say plus-or-minus-one) for the emulsifier system that will work best for you.

Suppose you find that an HLB of approximately 12 is optimum for your purpose. You might then make further tests around this value to establish this HLB value more accurately, i.e. these same two emulsifiers might be blended to try making emulsions at HLB values ranging step-wise between 11 and 13.

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 emulsion—the usual kind—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.

# 4

## CHAPTER

### Importance of Blending Emulsifiers and Choosing Ideal Chemical Type

Let's assume that you have determined the "Required HLB" of your ingredients as outlined in Chapter 3. Let's say it's 12.0. It might appear that the proper way to proceed now would be to obtain all the emulsifiers ICI-US 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. Actually, however, you must also find the *right chemical type* having the right HLB. Secondly, you're missing the opportunity the HLB System gives you to *tailor-make the ideal emulsifier for your own set of ingredients and conditions*. By blending two emulsifiers, 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 emulsifier 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. (For example, glyceryl monostearate, self-emulsifying grade, is actually a blend of *lipophilic* non-self-emulsifying g.m.s., with a *hydrophilic* soap or other substance to make it more water-soluble.)

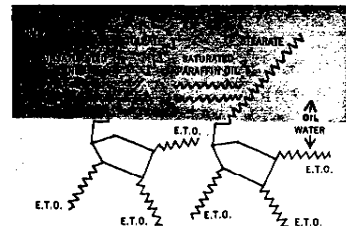
Only in relatively rare instances will you find a *single* emulsifier product to suit your requirements, even though it might have the exact HLB you need. Sometimes a complex blend is sold as a single emulsifier, and this might give you a somewhat better chance.

#### 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—but 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, palmittates 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 will have an HLB of about 12!)



The "chemical type" of an emulsifier blend is just as important as the HLB. For example, at left we see a polyoxyethylene sorbitan oleate water type of emulsifier blend with its unsaturated lipophilic oleate "tail" in the oil; an unsaturated chain like this seems to "attract" oils having unsaturated bonds. At right is another emulsifier blend, similar to the other except that it is a stearate; a saturated chain like this (or a laurate or palmitate) seems to "attract" saturated oil chains. Thus, although both types of oil might "require" an emulsifier having an HLB of 12, and both emulsifiers might have this HLB, the emulsifier that "attracts" the oil will be more effective.

# CHAPTER

# 5

## Calculating Ratio of Emulsifiers to Reach Any Desired HLB

Suppose, for example, that you used various blends of SPAN 60 and TWEEN 60 (stearates) to determine your "Required HLB," as was suggested to you in Chapter 3, and let's say you determined that your "Required HLB" is about 12.0. Now, you might like to try the *cleute* family of SPAN-TWEEN emulsifiers, i.e. SPAN 80 and TWEEN 80. How much of each do you need to give you an HLB of 12.0?

Here's an easy way to calculate how much of any emulsifier (A) to blend with any other emulsifier (B), to reach an HLB of X.

$$\% (A) = \frac{100(X - \text{HLB}_{(B)})}{\text{HLB}_{(A)} - \text{HLB}_{(B)}}$$

$$\% (B) = 100 - \% (A)$$

Using this formula to calculate how much SPAN 80 (HLB = 4.3) and how much TWEEN 80 (HLB = 15.0) you need to arrive at an HLB of 12.0, your calculation would be:

$$\% \text{ TWEEN 80} = \frac{12.0 - 4.3}{15.0 - 4.3} = \frac{7.7}{10.7} = 72\%$$

$$\% \text{ SPAN 80} = 100 - 72\% = 28\%$$

### HLB Computagraph

If you need to make many such calculations, you will find it more convenient to use the HLB Computagraph, illustrated in Figure 2. An HLB Computagraph is included in the center insert to be removed and used in a plastic cover or copied for your own calculations. On the reverse are precalculated values for surfactant blends.

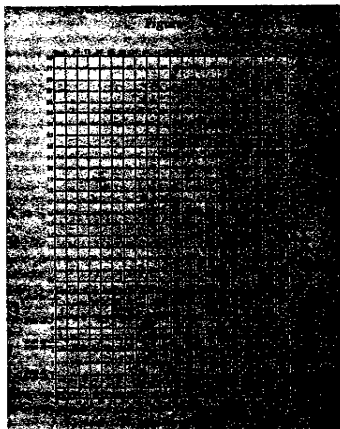
In Figure 2, HLB values of the SPAN group are marked along the left edge; those of the TWEEN group along the right edge; and percentage of TWEEN is shown from 0 to 100 across the bottom. If you're working with SPAN 20 and TWEEN 20, for instance, you merely draw a ruler line from the HLB value of one to the HLB value of the other; then you draw a horizontal line for the HLB value you want your blend

to have. By drawing a perpendicular line through the intersection of your two previous lines, you can read off the percentage of TWEEN you need, at the top or bottom of the graph.

You can enter the HLB values of any emulsifiers you wish along the left and right margins to compute HLB of any desired blend.

### Blends are Usually Best

We re-emphasize here that *blends* of emulsifiers are nearly always much more effective as emulsifiers than any single chemical composition would be. Therefore, when you have found the "Required HLB" for your



## HLB COMPUTAGRAPH

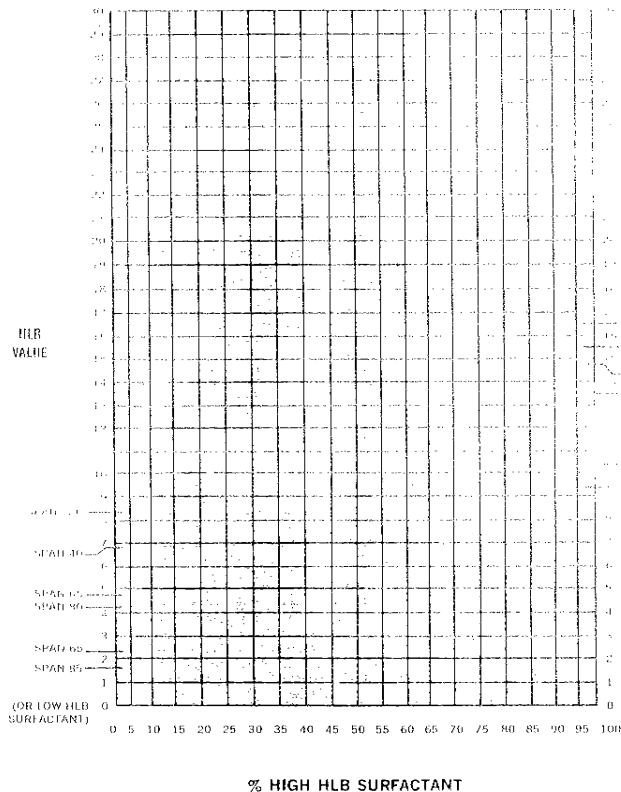
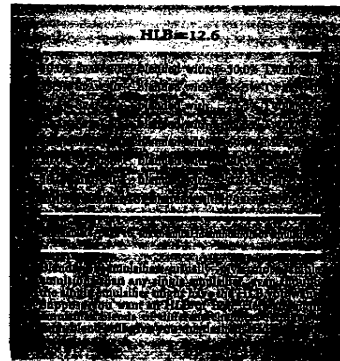


Figure 2. HLB Computagraph. Use copier or insert in plastic cover for your own calculations.

HLB VALUES OF BLENDED ATLAS SURFACTANTS

	100%	90%	80%	70%	60%	50%	40%	30%	20%	10%	0%
SPAN 20/TWEEN 20	1.8	2.2	2.7	3.2	3.7	4.2	4.7	5.2	5.7	6.2	6.7
SPAN 40/TWEEN 40	3.7	4.7	5.7	6.7	7.7	8.7	9.7	10.7	11.7	12.7	13.7
SPAN 60/TWEEN 60	4.7	5.7	6.7	7.7	8.7	9.7	10.7	11.7	12.7	13.7	14.7
SPAN 80/TWEEN 80	5.7	6.7	7.7	8.7	9.7	10.7	11.7	12.7	13.7	14.7	15.7
BRIJ 30/BRIJ 35 OR BRIJ 30 SP/BRIJ 35 SP	9.7	10.7	11.7	12.7	13.7	14.7	15.7	16.7	17.7	18.7	19.7
BRIJ 32/BRIJ 38	11.7	12.7	13.7	14.7	15.7	16.7	17.7	18.7	19.7	20.7	21.7
BRIJ 72/BRIJ 78	13.7	14.7	15.7	16.7	17.7	18.7	19.7	20.7	21.7	22.7	23.7
BRIJ 92/BRIJ 98	15.7	16.7	17.7	18.7	19.7	20.7	21.7	22.7	23.7	24.7	25.7

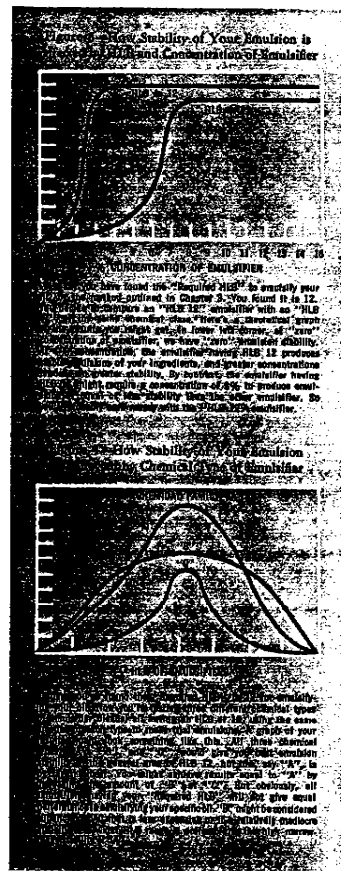


own set of ingredients, don't blindly assume you should now try every single emulsifier you can find that happens to have this HLB value!

#### Preliminary Step in Finding Ideal Chemical Type

Just to give yourself some idea of a systematic procedure for determination of the best chemical type to suit your problem, it is suggested that you try blends of other SPAN-TWEEN combinations. For example, if you determined your "Required HLB" of 12 by trying SPAN 60 blended with TWEEN 60, you might now try blending SPAN 20 with TWEEN 20 (laurates); then try the "40" combination (palmitates); then the "80" combination (oleates). Only one blend of each is necessary—the blend having an HLB of 12. You can compute this blend easily by algebra or with the HLB Computograph.

You may find that oleates give you the best "feel," while stearates give you best viscosity control. At the same time, perhaps the laurates give you an emulsion of satisfactory stability at extremely low emulsifier concentration, so maybe you could save money by using them. These preliminary findings might well guide you toward later experimentation with certain members of other chemical groups, if necessary. Likewise, you might find that you can obtain ideal results by blending one of the SPAN-TWEEN chemical types with another—say SPAN 20 with TWEEN 80.



# CHAPTER 6

## Investigation of Various Chemical Types

While the remaining steps in your emulsifier 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 a few trials of SPAN-TWEEN emulsifier combinations blended to meet your "Required HLB."

Your procedure now will be to try 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 type, but at least you have a reliable guide to 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.

### Tables 3 and 4 as Guides to Investigation of Chemical Types

After you have found the "Required HLB" of your oil phase under your own conditions, as discussed in Chapter 3, then Tables 3 and 4 on pages 14 to 17 make useful guideposts to the *chemical types* of emulsifiers you might try at your predetermined "Required HLB."

Examine Table 3 first, bearing in mind the application of your emulsion and the "Required HLB" you have previously found. In the left-hand column, you will find dozens of emulsifier applications in which ATLAS emulsifiers are often used. In the second column is the reference number of any single surfactant suggested for this application. In the third column is the reference number of various *blends* of surfactants suggested for trial. Also included here is the HLB range suggested for trial of surfactant blends. Your own "Required HLB" will likely fall within this range.

If possible, find your own application in Table 3, or one as nearly like it as you can. Find the reference

numbers of surfactants and surfactant blends suggested for this application.

Now turn to Table 4 and look up these references. Here you will find the trade name and chemical identity of the ATLAS surfactants or surfactant blends which ICI-US would suggest for trial *first*, based on our past experience. This is merely a suggestion, however, because your own emulsion or formulation problem may be different in many respects from the particular examples with which we have had experience in our own laboratories. These suggestions will guide you not only to specific surfactants, but also to the broad "chemical families" they represent.

Table 4 shows only about half of the total ICI-US "line" of surfactants. Many other surfactants in each of the chemical classes shown in Table 4 will be found in the booklet "General Characteristics of ATLAS Surfactants" (O-1).

To see how you can make best use of these surfactant suggestions, let's look at an example in which both a single surfactant and a blend are suggested.

Let's say you're trying to formulate an O/W antiperspirant cream. In Table 3, under "*Cosmetics*," you find that a typical single surfactant for this purpose is No. 131, and typical blends suggested are No. 551 and the 600 Class.

Now, turning to Table 4, you find that No. 131 is ARLACEL 165, of the glycerol mono- and di-stearate class, a blend of mono- and diglycerides with polyoxyethylene stearate. Its HLB is around  $11.0 \pm 1$ . In your previous tests to find the "Required HLB" of your own ingredients, you probably found that you need a surfactant having an HLB more like 16 to 17, for your typical stearic acid based cream. So, you might conclude that No. 131 does not fit your needs. In this particular case, however, the glycerol monostearate portion of the ARLACEL 165 would also serve as part of the waxy portion of your cream, so that, by using less stearic acid (as is the usual practice in making mono-

glyceride-based creams) ARLACEL 165 becomes a logical candidate for your trial.

No. 131 itself suggests that you might try other blends of the same nature as No. 131, i.e. blends of other mono- and diglycerides (Class 100) with polyoxyethylene stearates such as those in Class 500, many more examples of which may be found in the ATLAS Surfactant Catalog (O-1).

What about the No. 551 suggestion? In Table 4, you find that this is a blend of No. 501, MYRJ 52 polyoxyethylene stearate, with No. 703, G-2162 p.o.e. oxypropylene stearate. The HLB range in which these two products can be blended is narrow, from 16 to 17. If this fits the "Required HLB" you need, then you have a good candidate for trial—you can blend the two to fit any "Required HLB" from 16 to 17. Since they are both stearates, it might be a good idea to try other stearate blends of the 500 Class with the 700 Class.

What about the Class 600 suggestion? Looking at Table 4, you find that only No. 602, BRJ 35, is likely to give you an HLB high enough for your purpose. Blend No. 651 also looks promising for evaluation.

Going beyond the suggestions given in Table 3, since you know the "Required HLB" you need, you can easily spot on Table 4 a number of other blends that offer possibilities for trial, merely by looking for bars that cross the HLB 16-17 region. For example, Nos. 251, 253, 256, 351 and 371 might be found to give sufficiently stable emulsions with interesting other effects.

### Notes on Chemical Classes in Table 4

Examining the nine main chemical classes of ATLAS surfactants shown in Table 4, you will find that there are logical relations and interpolations between these classes. Classes 100 and 200 are generally lipophilic products. Classes 300, 400, 500 and 700 are generally hydrophilic. Classes 100 to 500, and 700 contain ester linkages and, therefore, are not ordinarily alkali stable. Class 600 covers a wide range of HLB and is alkali stable. Class 800 includes cationic and anionic surfactants. Class 900 products are, in general, blends of surfactants prepared for particular industrial applications. Reasonable cross-blending of classes should be tried in your emulsion research program.

Also, there are chemical types within these major classes. For example, adherence to a given fatty acid base is preferable, once the best one has been established.

Note that while reference is made to a single emulsifier, or to a specific blend, this is only a suggestion and the actual recommendation is to the entire class (and to related classes) of surfactants.

When considering various chemical types, you should always blend back to your required HLB value. How you may do this is apparent in Table 4. Here both single surfactants and some typical blends are illustrated. Blends of any two (or three or more) surfactants may be made (with the general exception of blending anionics and cationics).

The "blends" listed under each chemical class (such as 151, 251, etc.) are *not* for sale in the form of these blends, but are shown here to illustrate how two or more single products can be blended to reach any desired "Required HLB" that falls within the range indicated by the bar to the right of the designated blend.

### Emulsifier Suggested for Foods

All of the surfactants listed in Table 3 as suggestions for food products are either recognized by F.D.A. for use in certain foods or are GRAS (Generally Recognized as Safe).

The question might be asked "Why are so many single surfactants suggested here, when blends are usually best?" The reason is that foods and food ingredients from natural sources contain natural emulsifiers. Those shown in Table 3, when added, therefore, produce complex blends.

In some cases it may be found that the HLB of a suggested surfactant or blend does not match the "Required HLB" you have previously found for this food application. Usually this is because no "edible" surfactant of sufficiently high HLB is recognized for this application. Remember, however, that a sufficient quantity of an "off" HLB emulsifier will "work," even though not as efficiently or in as low a quantity as would a surfactant of the proper "Required HLB." (See Figure 3, Chapter 5.)

### Always Best to Find "Required HLB" First

Obviously, you can make good use of Tables 3 and 4 without ever having bothered to determine the "Required HLB" for your own particular emulsion system by the procedure shown in Chapter 3. However, you will find in the long run that you save much time and money if you take the trouble to follow the Chapter 3 system. Even if your formula should happen to be identical to those in our experience which led to the recommendations in Table 3, you could be misled by following the suggestions in Tables 3 and 4 alone, because of possible variations in characteristics of the oils and waxes that you employ, differences in manufacturing techniques, and especially differences in observation of desired properties.





Table 4—Typical Chemical Classification of ATLAS Surfactants for Reference from Table 3

Reference Number	Surfactant Identity	H L B												
		0	2	4	6	8	10	12	14	16	18	20	23	30
<b>Class 100—Mono and diglycerides</b>														
101	ATMOS 150, palmitate-stearate													
102	ATMOS 300, oleate													
111	*ATMUL 80, oleate-palmitate													
112	*ATMUL 84, stearate													
113	*ATMUL 124, stearate													
114	**ATMUL 500, stearate-oleate													
131	**ARLCEL 165, stearate													
132	ARLCEL 186, oleate													
141	***TWEEN-Mos 100, stearate-oleate													
Blends of:														
151	ATMUL 80/SPAN 60/TWEEN 60													
152	ATMOS 300/TWEEN 80													
153	ATMUL 80/TWEEN 60												*	
154	ATMOS 150/TWEEN 60													
155	ATMOS 150/SPAN 60/TWEEN 60													
<b>Class 200—Sorbitan fatty acid esters</b>														
201	***ARLCEL 20 or SPAN 20, laurate													
202	ARLCEL 40 or SPAN 40, palmitate													
203	ARLCEL 60 or SPAN 60, stearate													
204	ARLCEL 65 or SPAN 65, stearate (tri)													
205	ARLCEL 80 or SPAN 80, oleate													
206	ARLCEL 85, oleate (sesqui)													
207	ARLCEL 85 or SPAN 85, oleate (tri)													
216	ARLCEL C, oleate (sesqui)													
Blends of:														
251	SPAN 20/TWEEN 20													
252	SPAN 60/TWEEN 60													
253	SPAN 80/TWEEN 80												*	
254	SPAN 85/TWEEN 85													
255	SPAN 20/ARLCEL C/TWEEN 20													
256	SPAN 60/SPAN 80/TWEEN 20													
257	SPAN 60/SPAN 80/TWEEN 60													
<b>Class 300—Polyoxyethylene sorbitan fatty acid esters</b>														
301	TWEEN 20, laurate													
309	TWEEN 21, laurate													
302	TWEEN 40, palmitate													
303	TWEEN 60, stearate													
304	TWEEN 61, stearate													
305	TWEEN 65, stearate (tri)													
306	TWEEN 80, oleate													
307	TWEEN 81, oleate													
308	TWEEN 85, oleate (tri)													
Blends of:														
351	TWEEN 20/SPAN 20													
352	TWEEN 40/SPAN 40													
353	TWEEN 60/SPAN 60												*	
354	TWEEN 80/SPAN 80													
361	TWEEN 60/SPAN 80													
362	TWEEN 60/SPAN 85													
363	TWEEN 61/SPAN 80													
364	TWEEN 80/SPAN 60													
371	TWEEN 60/MYRJ 52													
381	TWEEN 60/TWEEN 61													
382	TWEEN 81/TWEEN 85													
393	TWEEN 60/TWEEN 65													
<b>Class 400—Polyoxyethylene sorbitol esters</b>														
401	ATLOX 1255, mixed resin and fatty acid													
402	ATLOX 1256, mixed resin and fatty acid													
411	ATLAS G-1086, oleate													
412	ATLAS G-3284, tallow													
421	ATLAS G-1702, beeswax													
422	ATLAS G-1726, beeswax													
423	ARLATONE T, oleate													
424	ATLAS G-1471, lanolin derivative													
425	ATLAS G-1471, lanolin derivative													

\*Available from vegetable source raw materials

\*\*Blend of mono- and diglycerides and polysorbate 80

\*\*\*These ARLCEL emulsifiers are especially light-colored (peroxide bleached) SPAN type products.

Reference Number	Surfactant Identity	H L B												
		0	2	4	6	8	10	12	14	16	18	20	23	30
<b>Class 500—Polyoxyethylene acids</b>														
501	MYRJ 52, stearate													
502	MYRJ 45, stearate													
505	MYRJ 55, stearate													
506	MYRJ 50, stearate													
521	RENEX 20, mixed resin and fatty acids													
Blends of:														
551	MYRJ 52/ATLAS G-2162													
<b>Class 600—Polyoxyethylene alcohols</b>														
601	BRJ 30, lauryl													
602	BRJ 35, lauryl													
603	BRJ 52, cetyl													
604	BRJ 56, cetyl													
605	BRJ 58, cetyl													
606	BRJ 72, stearyl													
607	BRJ 76, stearyl													
608	BRJ 78, stearyl													
609	BRJ 92, oleyl													
610	BRJ 95, oleyl													
611	BRJ 98, oleyl													
612	BRJ 98, oleyl													
613	BRJ 97, oleyl													
614	BRJ 99, oleyl													
615	BRJ 30SF, lauryl													
616	BRJ 55SF, lauryl													
631	RENEX 30, tridecyl													
632	RENEX 31, tridecyl													
633	RENEX 36, tridecyl													
Blends of:														
651	BRJ 30/BRJ 35													
652	BRJ 52/BRJ 56													
653	BRJ 56/BRJ 98													
654	BRJ 72/BRJ 76													
655	BRJ 72/BRJ 78													
656	BRJ 30/SPAN 85													
657	BRJ 56/BRJ 58													
661	RENEX 31/RENEX 36													
<b>Class 700—Polyoxyethylene adducts n.o.c.</b>														
701	ATLAS G-1288 fatty glyceride													
702	ATLAS G-1292 fatty glyceride													
703	ATLAS G-2162 oxypropylene stearate													
704	ARLATONE G, fatty glyceride													
<b>Class 800—Ionic surfactants</b>														
801	ATLAS G-3500 alkyl aryl sulfonate													
821	ATLAS G-263 N-cetyl-N-ethyl morpholinium ethosulfate													
822	ATLAS G-271 N-coryl-N-ethyl morpholinium ethosulfate													
Blends of:														
851	ATLAS G-3500/RENEX 20													
852	ATLAS G-3500/ATLAS G-1086													
853	ATLAS G-3500/ATLAS G-1292													
854	ATLAS G-3500/BRJ 98													
871	ATLAS G-263/SPAN 80													
<b>Class 900—Specialty surfactants</b>														
901	ATLOX 3355, nonionic-anionic blend													
902	ATLOX 3403, nonionic-anionic blend													
904	ATLOX 3404, nonionic-anionic blend													
904	ATLOX 3409, nonionic-anionic blend													
911	ATLAS G-2090 p.o.c. fatty amine-p.o.c. sorbitol oleate blend													
912	ATLAS G-2684 sorbitan oleate-p.o.c. esters of mixed fatty and resin acids blend													
Blends of:														
951	ATLOX 3403/ATLOX 3404													
952	ATLOX 3404/ATLOX 3409													
953	ATLOX 3403/ATLOX 3404/ATLOX 3409													

\* Dark portion of long HLB range bars indicates portion of range less likely to be useful for these blends as referred to from Table 3, although HLB's throughout the entire range of the bar may be attained by blending the indicated products.

## CHAPTER

# 7

### How to Determine HLB of an Emulsifier

What is an HLB number, and how does ICI-US determine it? The number itself, in the ICI-US system for most ATLAS nonionic emulsifiers, is merely an indication of the percentage weight of the hydrophilic portion of the nonionic emulsifier molecule. Thus, if a nonionic emulsifier were 100% hydrophilic, you would expect it to have an HLB of 100. In the ICI-US 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.

With this in mind, when you see that an ATLAS emulsifier such as TWEEN 20 polyoxyethylene (20) sorbitan monolaurate has an HLB value of 16.7, you know that it is about 84% hydrophilic. Theoretically, this HLB value may be calculated: the mol weight of TWEEN 20 is 164 (sorbitan) + 200 (lauric acid) + 880 (20 mols ethylene oxide) - 18 (water of esterification) = 1226. The mol weight of the hydrophilic portion (sorbitan + ethylene oxide) would be 164 + 880 = 1044. The HLB of TWEEN 20, i.e. 1/5th of the percentage weight hydrophilic portion, would thus be  $1044/1226 \times 100 \times 1/5 = 17.0$ . The published HLB value of 16.7 is obtained from actual analytical data, as explained below.

HLB values for most nonionic emulsifiers can be calculated from either theoretical composition or analytical data. The "theoretical composition" method may

lead to considerable error, 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. For example, HLB values of most polyol fatty acid esters can be calculated with the formula:

$$\text{HLB} = 20 \left( 1 - \frac{S}{A} \right)$$

where S = sap. number of the ester<sup>(1)</sup>

A = acid number of the recovered acid<sup>(2)</sup>

Example: TWEEN 20 polyoxyethylene sorbitan mono laurate

S = 45.5 avg.

A = 276 (for a commercial lauric acid)

$$\text{HLB} = 20 \left( 1 - \frac{45.5}{276} \right) = 16.7$$

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:

$$\text{HLB} = E/5$$

where E = weight percent oxyethylene content<sup>(3)</sup>

(1) AOCs Cd 3-25

(2) AOCs Cd 2-38 and AOCs L3a-57

(3) Morgan, F. W., Determination of Ethers and Esters of Ethylene Glycol, Ind. and Eng. Chem., Anal. Ed., Vol. 18, page 300, 1946.

#### Experimental Method of Determining HLB

While the formulas given above 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 ATLAS 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 5.



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## CHAPTER

## 8

*Step-by-Step Summary*

**Step-by-Step Outline of HLB System for Selecting Emulsifiers . . .** *The previous seven chapters have discussed details of the HLB System for selecting emulsifiers. The following is a brief summary of this system.*

**Step One**

Determine the "Required HLB" for the oil or other ingredients you wish to emulsify. Chapter 2 shows the "Required HLB" for 50 different oils, waxes, etc., and an easy method for calculating any combination of these 50. Chapter 3 shows how to experimentally determine the "Required HLB" for any combination of ingredients, including unknown oils or waxes in water which might contain electrolytes.

**Step Two**

Try different chemical types of ATLAS emulsifier blends, adjusted close to the "Required HLB" you found in STEP ONE. You save time because you don't

need to try any other blends than those at your predetermined "Required HLB." Chapter 5 discusses a preliminary investigation of chemical types, using combinations of SPAN and TWBEN emulsifiers. Chapter 6 suggests several other blended combinations of ATLAS emulsifiers for trial. Chapter 5 shows how to calculate the ratio of any two ATLAS emulsifiers to reach your "Required HLB."

**Step Three**

If your emulsion experience indicates trial of other chemical types of emulsifiers than those made by ICI-US, you can still save much time by determining the HLB of these emulsifiers, by methods shown in Chapter 7. If one specific familiar emulsifier does not have your "Required HLB" (as determined in STEP ONE), then you should blend it with another emulsifier to obtain this "Required HLB" for optimum results.



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**ANTICIPATING NEEDS**