

CLASSIFICATION OF SURFACE-ACTIVE AGENTS BY "HLB"[†]

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SINCE THE INTRODUCTION of the "HLB" system of classifying and selecting emulsifiers (6) numerous requests have been received concerning its derivation. The term "HLB" comes from the words hydrophile-lipophile balance. Emulsifiers consist of a molecule that combines both hydrophilic and lipophilic groups (or polar and non-polar groups) and it is the balance of the size and strength of these two opposing groups that we call HLB.

Surface-active agents have been classified in many ways: including chemical types and according to ionization. Classification by HLB permits some prediction of behavior and reduces the amount of work involved in the selection of an emulsifier, wetting agent, or other type of agent.

Emulsifiers constitute one of the widest used subdivisions of surface-active agents and we will use this group as an illustration of the manipulation of the HLB system, with reference to other applications later.

A complete system for selecting an emulsifier would provide the *best* emulsifier to give the *desired form* of product for the desired *raw materials*. Thus, knowing the materials to be emulsified, the *most efficient* emulsifier could be chosen for the desired type of emulsion.

ACTION OF EMULSIFIERS

An emulsifier has two actions that are distinctly different. The accepted action is that of promoting the formation of an emulsion; making the emulsion easier to prepare; producing a finer particle size; and aiding the stability of the emulsion. The second action, which occurs along with the preparation of the emulsion, consists in controlling the type of emulsion that is to be formed, O/W or W/O. This second action appears to be a function of HLB.

In evolving a system for the selection of emulsifiers, we will first consider briefly the theory of emulsification. For practical purposes, an emulsion consists of two immiscible liquids, one being dispersed as a multitude of small particles in the

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other. The former is called the dispersed phase and the latter is called the continuous phase. Industry demands further that an emulsion must exhibit a certain stability under a variety of conditions. Emulsifiers and stabilizers are added to attain the desired stability.

Between the two phases of an emulsion, a large area or interface exists which surrounds each particle. The adsorption of emulsifiers at the emulsion interface has been established. The nature of this interface, whether mono- or multi-molecular in thickness, is still in question as pointed out by Schwartz and Perry (5) in their new book.

Since the particles of an emulsion are considerably larger than molecular in size, we may consider the interface that surrounds each particle as being similar to the interface which separates the phases when present in bulk. If we were to shake mineral oil with water we obtain an emulsion that will break quickly into its two phases. Examination of the interface would reveal that the interfacial tension is high, approximately 45 dynes/cm. With the addition of an emulsifier of suitable type this would drop to almost zero. This reduction in interfacial tension primarily assists in forming the emulsion though it also promotes stability.

As mentioned above, the assistance in emulsion formation and subsequent stabilization appears to be only part of the action of an emulsifier. In addition, the emulsifier usually establishes the type of

emulsion formed. In our study and use of emulsifiers, it appears that the action of emulsifiers may be related to their structure roughly as follows:

First, "what the emulsifier or surface-active agents will do," that is, make an O/W or W/O emulsion, act as a detergent, or solubilize an oil, or have some other action, seems to depend on what we call the HLB of the emulsifier. This value is an expression of the relative simultaneous attraction of an emulsifier for water and for oil (or for the two phases of a system to be emulsified). Emulsifiers consist of a molecule that combines both hydrophilic and lipophilic groups and it is the balance of the size and strength of these two opposing groups that we call HLB. For purposes of convenience, the effective balance of these groups is assigned a numerical value.

Second, how efficiently the emulsifier will work seems to be related to over-all chemical structure, that is, whether the emulsifier is a soap, a partial ester, a complete ester, whether the lipophilic group is saturated, and so forth. This latter action appears to be quite specific and no "rules" have been established.

DEVELOPMENT OF HLB SYSTEM

In our present system, an emulsifier that is lipophilic in character is assigned a low HLB number and an emulsifier that is hydrophilic in character is assigned a high number. The midpoint is approximately ten

and the assigned values have ranged from one to forty. When two or more emulsifiers are combined or blended, the HLB values are additive in behavior. Thus, if we blend three parts of emulsifier "A" having an HLB of 8 and one part of an emulsifier "B" having an HLB of 16, the resulting HLB of the blend will be the sum of three-quarters of 8 and one-quarter of 16, i.e. $(6 + 4)$ or 10.

We should note that chemical type alone does not establish hydrophile-lipophile balance. Thus, soaps may range from strongly hydrophilic for sodium laurate to strongly lipophilic for aluminum oleate; esters, ether-esters, and ethers may range from low to high HLB's, sulfates and sulfonates may range from medium to high.

HLB is not the same as solubility, though there is an over-all relationship. Thus, materials having low values *tend* to be oil soluble and materials having high values *tend* to be water soluble. However, two emulsifiers may have the same HLB and exhibit different solubility characteristics.

In the preparation of an emulsion, the reduction of interfacial tension makes it easier to disperse one of the phases in the other. The nature of the interface established by the adsorption of the emulsifier at the interface in some manner influences the two immiscible liquids to such an extent that one breaks up into droplets while the other retains its continuity. The interface apparently "bends" more easily in

one direction than the other. This would seem to decide the type of emulsion that is formed—whether O/W or W/O. Presumably, the behavior of an emulsion could be expressed by observing the proper characteristics of this interface.

It occurred to us that the "bending" tendency of the interface might be observed by determining the interfacial tension in different directions (i.e., up and down), from one phase to the other and *vice versa*. A literature search revealed that Roberts (4) had already made a brief study of this effect in relation to natural petroleum emulsions. In his work, differences in interfacial tension were observed whether the duNouy ring was pulled up or pushed down through the interface. However, the existence of a difference in interfacial tension is questioned since interfacial tension is in itself the difference in free energies of the two phases. It is possible that the observed differences are due to the introduction of a third phase, the platinum ring. Whether or not this is true, with efficient emulsifier systems, observations are most difficult because, by their very nature, these systems have an interfacial tension of almost zero (since they form emulsions spontaneously) and therefore the precision of measurement is low. Hence, this phase of the study was not considered further.

Other experimental means of estimating HLB have been considered. Lambert and Busse (2) recently published a rapid method of deter-

mining the "dye solubilization" efficiency of surface-active agents as previously described by McBain (3). A comparison of our estimated HLB values and some of the data published by Lambert and Busse is most interesting. In their derivation of an equation for a solubilizing isotherm, n and K are constants which are characteristic for each agent. In Table 1 we compare HLB values and

TABLE 1

Agent	n (2)	$\log K$ (2)	Estimated HLB
Igepal CA	0.80	0.19	12.8
Emulphor ELA	0.83	0.31	13.3
Emulphor ON	0.95	0.11	15.4
Sodium Oleate	1.06	0.24	18

their data for n and K for several agents. While there is no apparent relationship between HLB and K , there is remarkable agreement between HLB and n . This is being studied further in an effort to establish the existence of the agreement. However, until this or some other system of estimation is devised, estimation by cross reference of a large number of emulsification tests with established materials appears to be the most satisfactory, though laborious, method.

Our original estimation of empirical HLB values for many Atlas surface-active agents was based on results observed in a large number of emulsification studies conducted over several years. These studies were predominately of O/W emulsions. We found that the emulsi-

fiers most often used as O/W emulsifiers had assigned HLB values within the range of about nine to twelve. The values of our surface-active agents used for other purposes were then correlated, with the results shown in Table 2. After

TABLE 2

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

we had conceived the idea of HLB as applied to our own materials and had assigned values to many of them we began investigating expansion of the idea's usefulness.

The Atlas Span and Tween emulsifiers had found their way into industry as detergents, wetting agents, etc., by every conceivable method and there were a multitude in the development stage aimed at these various uses. When our laboratory began correlating HLB of industrially used compounds and development stage materials *versus* their use, there occurred a self-alignment that was remarkable to see.

One could appreciate the potential advantages of any method whereby we could connect HLB data on our own materials to HLB data for all surface-active agents. Widely applied, this could simplify immensely the choice of emulsifiers for a given industrial task.

Consideration of these possibili-

ties led to the realization that here we may have a common denominator that would enable us to relate and pin together all surface-active agents regardless of type which heretofore at best were considered by groups.

ESTIMATION OF HLB VALUES FOR EMULSIFIERS AND OILS

In our proposed system, HLB values for new emulsifiers are estimated from a series of tests in which actual emulsification behavior is compared. Comparison, by means of blends or mixtures, is made with agents of known HLB values, such as the series of Atlas emulsifiers. Emulsifiers, as used in industry, are almost always blends. The blend is usually most efficient if it combines lipophilic and hydrophilic emulsifiers. We usually recommend that Span* and Tween* emulsifiers be used blended. Glyceryl monostearate, self-emulsifying grade, is a blend. Even the monovalent soaps, generally used for O/W emulsification, are blends of soap and hydrolyzed fatty acid.

Variation of the proportions of the blended emulsifiers has been taught as preferred practice to obtain best results. When two emulsifiers of known HLB are thus blended for use with a given oil there is an optimum ratio that gives best emulsification and the HLB at this ratio is said to be the required HLB for the oil (to give that type of emulsion, whether O/W, W/O solubilization, etc.) This is expressed by the equation:

$$\frac{W_A HLB_A + W_B HLB_B}{W_A + W_B} \left(\begin{array}{c} \text{optimum} \\ \text{ratio} \end{array} \right) = \text{HLB oil}$$

wherein:

W_A = the amount (weight) of the first emulsifier (*A*) used, and

W_B = the amount (weight) of the second emulsifier (*B*) used at the "optimum ratio," giving the best emulsion

HLB_A, HLB_B = the assigned HLB values for emulsifiers *A* and *B*

HLB oil = the "required HLB" of the oil for the type of emulsion being studied

Since good emulsification may occur over a wide range of emulsifier ratios, or since emulsification in the entire series may be only mediocre, the optimum ratio may be obscured. By averaging results with several emulsifiers and several oils the estimation is made more precise. In conducting a number of these tests it will be apparent that the information will have relationship to many factors.

To establish the necessary cross relationships, series of emulsions were prepared over a standard formula. The emulsion in these tests were prepared in a uniform manner in so far as possible. Ten grams of emulsifier, or the appropriate amount of fatty acid for a soap, was weighed into an 8-oz., tall form, wide-mouthed jar. Ninety-five grams of oil, or molten wax, was added and the jar and contents agitated until the ingredients were well mixed. Ninety-five cubic centimeters of water was then added at one time (cold or hot depending upon the melting point of the oil or wax) and the jar capped and shaken. If required, alkali or amine is added

TABLE 3

Material	Trade Mark	Manufacturer or Distributor
Beeswax	Beehive Brand	Will and Baumer Candle Co., Inc.
Cetyl Alcohol	E. I. du Pont de Nemours & Co., Inc.
Cottonseed Oil	Wesson Oil	Wesson Oil and Snowdrift Sales Co.
Lanolin, anhyd., U. S. P.	Botany Mills, Inc.
Mineral Oil, heavy	Nujol	Stanco Distributors, Inc.
Mineral Oil, light	Marcol GX	Stanco Distributors, Inc.
Paraffin	Paraseal	Socony-Vacuum Oil Co., Inc.
Petrolatum, white	White Perfecta	L. Sonneborn Sons, Inc.
Stearic Acid, D. P.	Emersol 120	Emery Industries, Inc.

with the water. After a few minutes the emulsion was reshaken and then stored overnight. Storage was again either at room temperature for oils or at 60–70°C. for waxes. Observations (and pictures) were usually taken after twenty-four hours. Further storage appeared to affect results little. In a few cases the observations were taken before 24

hours due to the poor quality of of emulsions in an entire series. Since the data are comparative this is considered permissible when an entire series is handled as a unit. O/W or W/O emulsions may result and this behavior must be checked. Usually the difference is readily apparent, in fact is expected depending upon the HLB of the emulsifiers.

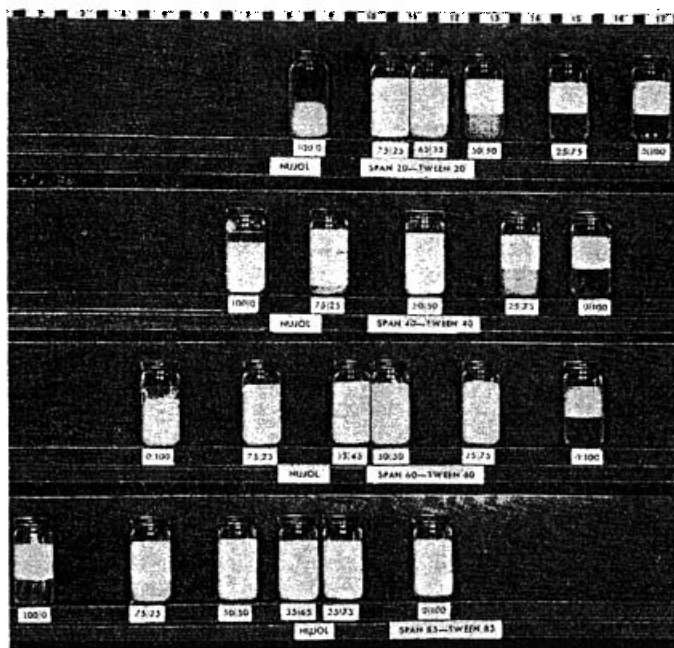


Figure 1.—Effect of ratio of low and high HLB emulsifiers on emulsification (the same weight per cent of emulsifier is not best)

The amount of emulsifier used in these tests, 10 gm. for 95 gm. of oil, is much more than is usually required to obtain emulsification. Usually in a given system, the degree of emulsification increases with increasing amounts of emulsifier to a point. Beyond this point, the addition of emulsifier does not improve or harm the emulsion. The high proportion of emulsifier was selected as providing maximum expected emulsification from the agents under test so that those having a poor over-all efficiency would indicate trends. The oils and waxes usually included in an evaluation series are listed in Table 3.

These values may be utilized more completely than for a gross estimate of the behavior of the emulsifier. In Fig. 1, we show several series of samples in which heavy mineral oil is emulsified with several combinations or blends of emulsifiers. In each series, the only difference is the types of emulsifiers employed. Two emulsifiers are used in each row, one having a low and one a high HLB. The samples on the extreme left are emulsified with 100% of low HLB agents; the samples on the extreme right are emulsified with 100% of high HLB agents. Blending permits coverage of the complete range of values between the two emulsifiers. From top to bottom, the emulsifiers are blends of laurate, palmitate, stearate, and oleate ether-esters (the latter in addition being tri esters). You will note that the weight percentages of the low and high HLB

products required are not similar for best emulsification and that the

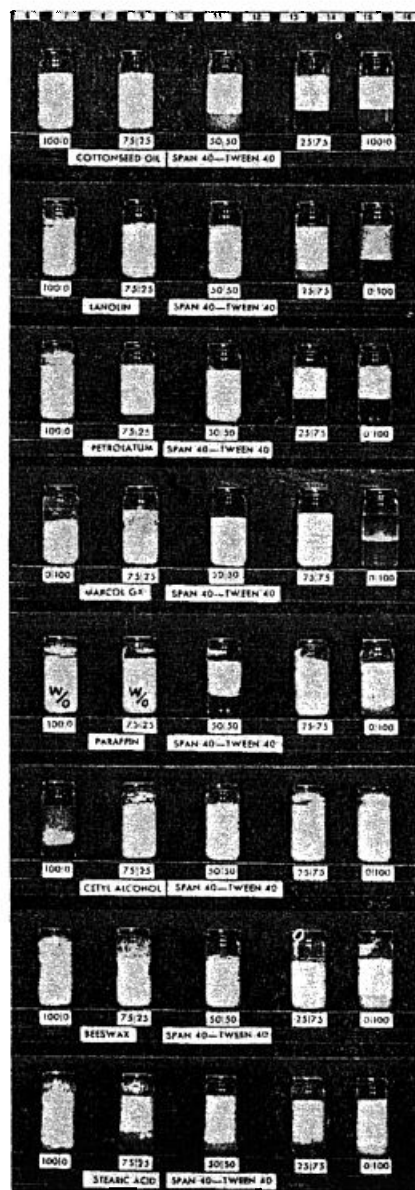


Figure 2.—Behavior of various oils with one pair of emulsifiers (different ratios best for different oils)

gross efficiency of the systems are not identical. The important fact to us is that in each instance, the best emulsion is obtained at about an HLB of 10. This is one of the major points on which this system is based. A given oil has an optimum HLB for a given type of emulsification.

Different oils require different values as may be seen in Fig. 2. In

The optimum required HLB values indicated in Fig. 2 were for O/W emulsions. It will be noted that at times a W/O emulsion is formed. This usually appears at the extreme left-hand side of the figure. When this occurs, the oil is suitable for use in W/O formulations in major amounts. Often good emulsions are obtained of both types and the oil can have an optimum HLB for either type of emulsion.

When we speak of a required HLB, reference is usually made to the O/W type. Fortunately, the range covered by the inverse or W/O type appears to be quite narrow and in the low HLB's so that the difference is readily apparent.

Required HLB values for blends of oils may be calculated in a manner similar to that for blends of emulsifiers so long as the requirements for the components are known.

Basis for this is illustrated in Fig. 3 in which all mineral oil is emulsified in the top row, 50/50 mineral oil-stearic acid in the middle row, and all stearic acid in the bottom row. The optimum emulsifier blend progresses from about 10 for 100% mineral oil to about 16 for 100% stearic acid.

A natural question is the adherence of the HLB system to ionic or soap emulsions. Monovalent soaps, generally used for emulsification, ex-

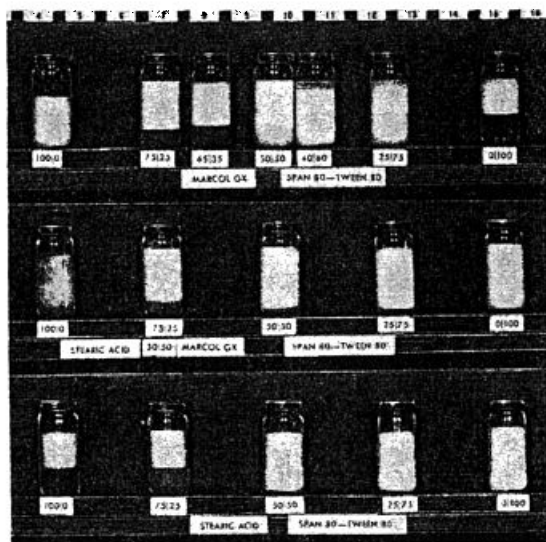


Figure 3.—Effect of blending oils and waxes

this figure, one of the pairs of non-ionic emulsifiers used in Fig. 1, Span 40-Tween 40, is pictured with eight different oils or waxes; cottonseed oil, lanolin, petrolatum, mineral oil, paraffin, cetyl alcohol, beeswax, and stearic acid. It will be apparent that to choose an emulsifier for a formula we need to know the *required* HLB for the oil blend, as well as that of the proposed emulsifiers.

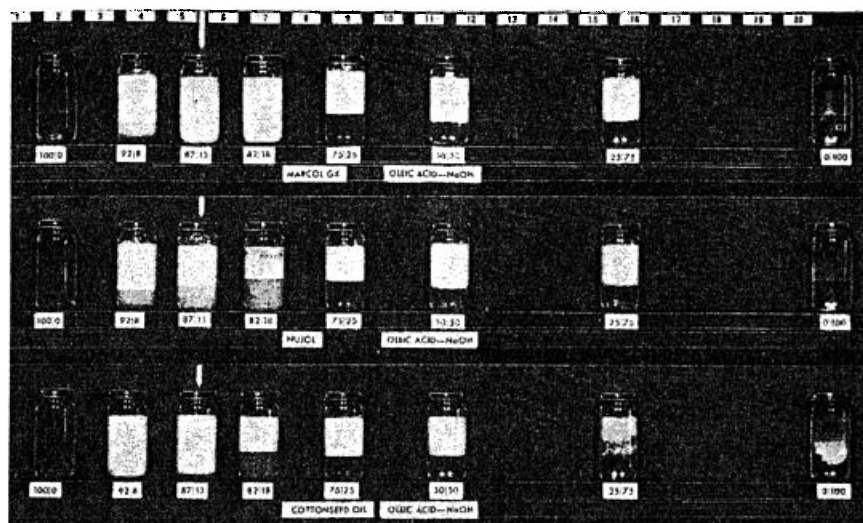


Figure 4.—Behavior of soaps—varying ratios of oleic acid and NaOH

hibit high HLB's, higher than required for optimum emulsification. However, soap alone is seldom, if ever, the sole emulsifier in a formula. We know that soaps hydrolyze, and the true emulsifier is a mixture, or blend, of soap and free fatty acid. This is illustrated in Fig. 4 where the samples with the arrows are the theoretically neutralized soaps, but in each instance, the samples to the left in which there is excess fatty acid are the better emulsions.

The emulsifier, so-called, in these series ranges from all fatty acid at the left to all base at the right. This might be considered as representing increasing HLB from left to right, though it is only true to a point slightly to the right of the theoretical soap. At this point sufficient base has been added to minimize hydrolysis of the soap. Any higher ratio of base to fatty acid merely results in a reduction of the

total amount of fatty acid and a reduction of the amount of soap.

Goodey (1) has studied the behavior of emulsifiers and has explained, in part, their action by defining a part of the emulsifier as a coupler. This is not coupling action as the word is generally used (the addition of an agent to promote clarity of solution of a concentrate or emulsion). He suggests that there are four constituents of an O/W emulsion: oil, water, emulsifier, and coupler. In his explanation, the emulsifier is always a highly hydrophilic substance and the coupler is always oil-soluble. The coupling action of which he speaks is promotion of solubility of the emulsifier in the oil phase to further the reduction of interfacial tension and improve emulsification. We prefer to consider all of this action under the term emulsification and to call both components emulsifiers.

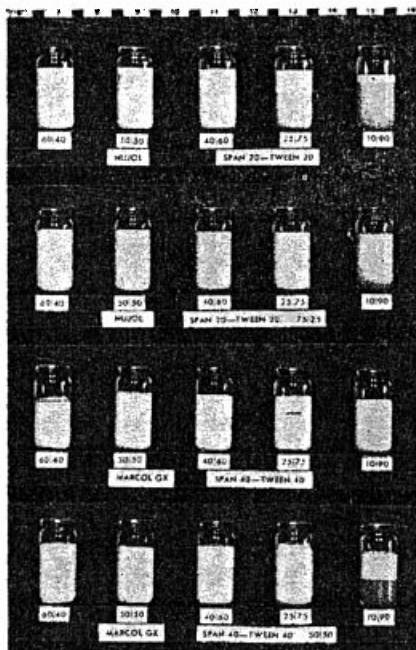


Figure 5.—Comparison of fixed “coupler” content *vs.* fixed HLB at different emulsion concentrations

Goodey's data and ours agree that the agents involved must have the proper hydrophile-lipophile balance. He suggests further that a proper hydrophile-lipophile balance for both the coupler and emulsifier is needed and that a given concentration of coupler is needed in the oil phase to “attract” the hydrophilic emulsifier to the interface. Therefore, a 20% oil emulsion would contain twice as much coupler as a 10% oil emulsion.

The emulsions in Fig. 5 indicate that this is not true. Rather, for a given oil and water there is one HLB for the total emulsifier that is best without regard to the concentrations of ingredients in the usual ranges. By way of illustration, the two pairs of series of samples contain various amounts of oil and water, the amount of oil decreasing

TABLE 4—PERCENTAGE COMPOSITION OF EMULSION IN FIG. 5

Sample No.		1	2	3	4	5
Row 1						
Oil		60	50	40	25	10
Water		34.3	45.0	55.8	71.9	88.05
Span 20	HLB 8.6	4.5	3.8	3.0	1.9	0.75
Tween 20	HLB 16.7	1.2	1.2	1.2	1.2	1.2
Row 2						
Oil		60	50	40	25	10
Water		34.0	45.0	56.0	72.5	89.00
Span 20	HLB 8.6	4.5	3.8	3.0	1.9	0.75
Tween 20	HLB 16.7	1.5	1.2	1.0	0.6	0.25
Row 3						
Oil		60	50	40	25	10
Water		34.5	45.0	55.5	71.2	87.0
Span 40	HLB 6.7	3.0	2.5	2.0	1.3	0.5
Tween 40	HLB 15.6	2.5	2.5	2.5	2.5	2.5
Row 4						
Oil		60	50	40	25	10
Water		34.0	45.0	56.0	72.4	89.0
Span 40	HLB 6.7	3.0	2.5	2.0	1.3	0.5
Tween 40	HLB 15.6	3.0	2.5	2.0	1.3	0.5

from left to right. The samples in the first and third rows were prepared with a *fixed percentage* of low HLB emulsifier in the oil phase to conform with Goodey's requirements for a "coupler." In the second and fourth rows, all of the samples had the same *ratio* of low and high HLB emulsifiers. The percentages are shown in Table 4. It is seen that a constant HLB for the total emulsifier provides a more uniform emulsification.

In Table 5 we have listed several estimated HLB values for emulsifiers. These were determined and correlated by preparing vast series of emulsifier-blend tests as in the illustrations. Grouping in this table is according to composition as well as HLB since both are influential in choosing an emulsifier. We hope to extend this list, and expect to do so. The magnitude of this type of study is understood when you realize that each of these values was derived from approximately 75 emulsions. A more extensive tabulation of estimated HLB values for Atlas products is available in the Atlas Surface Active Agents Booklet (6). We have found the chart, Fig. 8, most helpful for rapid calculation of HLB values of blends of emulsifiers. The location of glyceryl monostearate in Table 5 is of interest. This reference is to the pure form and not to the self-emulsifiable varieties. The available self-emulsifiable types are *not* non-ionic, since ionic emulsifiers (soap, etc.) are added to render them self-emulsifiable. This is an example of

a blend of non-ionic and ionic emulsifiers. These blends are satisfactory when no electrolytes antagonistic to the ionic portion of the blend are to be employed. In such cases a totally non-ionic emulsifier should be used.

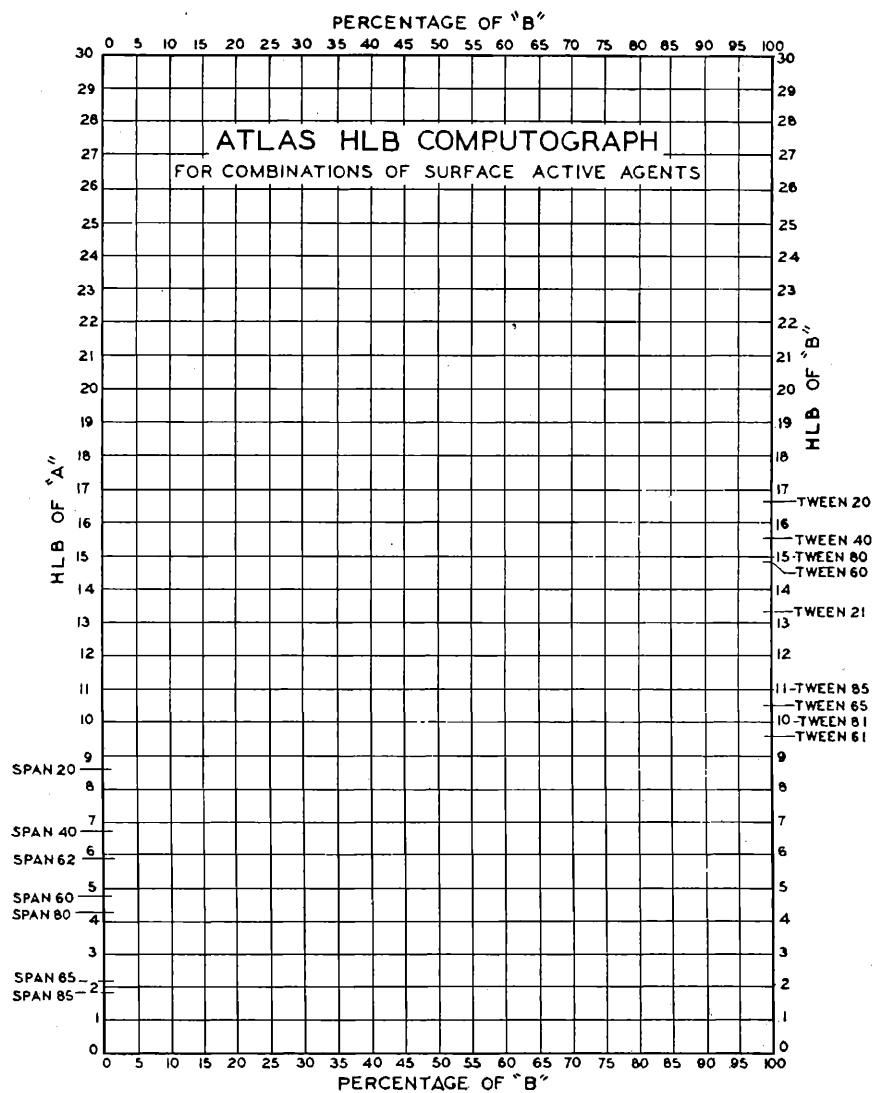
TABLE 5

Emulsifier	Estimated HLB
Anionic	
T. E. A. Oleate	12
Lecomene O	12.7*
Sodium Oleate	18
Potassium Oleate	20
Cationic	
Atlas G-251	25-35
Non-Ionic	
Oleic Acid	App. 1
Span 85	1.8
Arlacel C	3.7
Span 80	4.3
Span 60	4.7
Span 20	8.6
Tween 81	10.0
Tween 60	14.9
Tween 80	15.0
Tween 20	16.7
Other values listed in booklet, "Surface Active Agents," published by Atlas Powder Co.	

* Tentative value.

The various types of emulsifiers represented in Table 5 may be blended, observing the usual precautions of incompatibility. In addition, there are indications that some emulsifiers are not compatible, or perhaps co-operative is a better word, in a surface-active sense. This action is probably related to overall efficiency of the emulsifier and is therefore not conclusively indicated.

Chemical reactivity of an emulsifier can modify the behavior of an



SPAN, TWEEN: REG. U. S. PAT. OFF.

emulsifier immensely. In the case of soaps, traces of multivalent ions completely change the HLB. Another instance that we have observed was with an amine-neutralized aryl sulfate, where the presence

of acidic constituents lowered the HLB of the emulsifier markedly.

Likewise, in Table 6 we have listed the estimated required HLB values for several of the more commonly used oils and waxes. These

TABLE 6

Oil or Wax	Required HLB for	
	O/W Emulsion	W/O Emulsion
Cottonseed Oil	7.5	..
Carbontetrachloride	9*	..
Paraffin (household)	9	4
Microcrystalline wax (Micropac Q, S-V)	9.5*	?
Mineral Oil, White, light (Marcol GX)	10	4
Mineral Oil, White, heavy (Nujol)	10.5	4
Mineral Seal Oil	10.5*	?
Petrolatum, white (White Perfecta)	10.5	4
Silicone Oil (G. E.)	10.5*	?
Kerosene	12.5*	?
Naphtha	13*	?
Cetyl Alcohol	13	?
Orthodichlorobenzene†	13*	?
Beeswax, white	10-16	5
Carnauba Wax	14.5*	?
Candelilla Wax	14.5*	?
Lanolin, U. S. P., anhyd.	15	8
Dimethyl Phthalate	15*	?
Orthophenylphenol	15.5*	?
Stearic Acid	17	..

* Tentative.

† Plus small amounts (3.5%) of pine oil and isopropyl alcohol.

values are reported only in half-unit increments due to lack of precision in measurement. However, the values are amply accurate for use with the HLB values for the emulsifiers in a selection of an emulsifier combination. The oils and waxes are tabulated in ascending order of required HLB's. As would be expected similar values are noted for like chemical types.

METHOD OF USE OF HLB VALUES

We have developed a "refined trial-and-error system" based on HLB values. In any emulsification problem one of two conditions can exist: (1) the problem can be to emulsify an oil phase of unknown composition, or (2) the approximate desired formula may be known including the composition of the oil phase.

If the properties, particularly the required HLB, of the oil phase are unknown as in the first condition, a preliminary exploratory test is set up. This is usually done with a non-ionic emulsifier combination, such as Span 60 and Tween 60, of known HLB values.

The first series of determinations are prepared with various ratios of these emulsifiers using a maximum amount of total emulsifier. Usually a series, resembling those in the top row of Fig. 6, is obtained. It appears that the optimum HLB for this system is between samples 3 and 4. A more accurate determination of the required HLB is next obtained by the preparation of a second series, using small increments of this same pair of emulsifiers as shown in the second row of tests.

After determination of the opti-

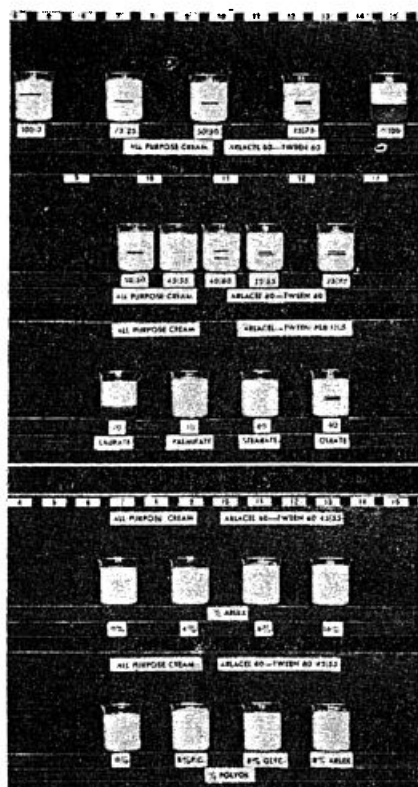


Figure 6.—Example HLB use emulsions, all-purpose cream

(Top Row) Preliminary determination of required HLB of oil phase. (Middle Row) Final estimation of required HLB, value 10.4. (Bottom Row) Comparison of various chemical types, all at same HLB

Figure 7.—Effect of polyol on all-purpose cream

(Top Row) Various amounts of Arlex. (Bottom Row) Various polyols.

At this point, the chemical classification for the emulsifier is studied by preparing a third test series, as in the third row, in which emulsifiers of selected different chemical types are tried, all of which have been previously blended to the required HLB. After choosing the chemical type, a final series usually suffices to provide a blend of emulsifiers of

the chosen chemical type at the most favorable HLB and at the minimum required total concentration. This last series of samples is usually put through more extensive and more stringent stability tests.

If the required HLB of the oil phase is known approximately, the first series of tests may be eliminated. If it is known with greater accuracy, both the first and second series of tests may be omitted.

For an example, an All-Purpose Cream has been chosen with a proposed formula of:

Beeswax.....	5
Mineral Oil.....	26
Hydrogenated Vegetable Oil.....	18
Polyol.....	4
Emulsifier.....	5-10
Water, <i>q. s.</i> to make.....	100

The oil phase, then consists of the following approximate percentages.

Oil or Wax	%	Estimated Re-quired HLB	% × HLB
Beeswax	10	15	1.5
Mineral Oil	53	10	5.3
Hydrogenated vegetable oil	37	9	3.3
Average estimated required HLB			10.1

Calculation of an estimated required HLB gives a value slightly over 10. Therefore, the initial series with this oil phase can be prepared combining Span 60 and Tween 60 to give HLB values close to 10, as in the second row, Fig. 6.

Span 60-Tween 60	Calculated HLB
50-50	9.8
45-55	10.3
40-60	10.8
35-65	11.3
25-75	12.4

The best ratio in this series is 45% Span 60 and 55% Tween 60 at a calculated HLB of 10.3.

The evaluation of different chemical types of emulsifiers is then considered as previously mentioned. For this example, the stearate blend is the best chemical type. Usually it will be desirable to cover a much wider range of alternate chemical types than the space limitation permitted us in the third row of Fig. 6. It must be remembered that all blends must be at the correct HLB.

It is interesting to note that the addition of polyol to the aqueous phase of an emulsion such as was just studied does not appear to alter the HLB appreciably. The samples in the top row of Fig. 7 show the effect of adding various amounts of commercial sorbitol sirup. The percentages are the amount of Arlex* in the total formula, not the amount in the aqueous phase. Therefore, for the fourth sample the aqueous phase contains approximately 40% polyol which is a sizable proportion. In the second row, three different polyols are employed. Little difference is noted in the emulsification, regardless of the type of polyol used. This does not imply that the three polyols will produce similar cosmetic effects. These differences are well known and are due to the variations in hygroscopicities, cosolubilities, and other physical properties of the polyols themselves. The data indicate that at the proper balance of emulsifier, the emulsification will not be appreciably af-

ected by the type and amount of polyol.

The dividing line between ingredients and emulsifiers is often not clear. Stearic acid, lanolin, cholesterol, and beeswax are just a few examples of materials that may serve a dual role. An example of this is in soap-emulsified-facial-creams in which the stearic acid is partially neutralized. In this, the stearic acid forms a bulk of the oil phase, but portions of the stearic acid are present as emulsifier, both neutralized and as free acid. By examining a system, it is usually possible to evaluate each ingredient in the terms of its uses.

APPLICATIONS OTHER THAN EMULSIFICATION

(1) *Antifoaming*

Antifoaming is quite a specific action, therefore it is surprising when most of the Atlas agents that have found success as antifoam agents fall in the range of 1.5-3 and all are less than 8. No complete study of this subject, as with emulsifiers, has been made or is contemplated.

(2) *Wetting and Spreading*

Atlas wetting and spreading agents fall in the rather narrow HLB range of 7 to 9. We have frequently tried products outside this range, but with little success, particularly when the values were greater than 9. Wetting is usually desired in an aqueous solution, suspension, or O/W emulsion, and this is probably the cause of the narrow effective

range. No extensive selection work has been done in this field.

(3) Detergents

Atlas detergent materials fall into the HLB range of 13–15. This range is in accord with recent theories of detergency that solubilizing of the soil is a part of the action since 13–15 is above the usual O/W emulsifier range and is close to solubilizers.

(4) Solubilizers

Solubilizing requires the highest HLB (for common uses) at 15–18. For this purpose, single high HLB agents are frequently used. Early work has indicated that the HLB can be too high for efficient solubilizing. The effective range appears to be narrow even for different oils. No thorough study of solubilizing *vs.* HLB has been undertaken.

SUMMARY

We have described a system for the choice of emulsifiers based on their hydrophile-lipophile balance. The HLB system, though it does not indicate the over-all efficiency

of the emulsifier, does tell "what it will do"—that is, what kind of an emulsion or product to expect. By so doing, it enables us to compare various chemical types of emulsifiers at their optimum balance. Estimated HLB values for various types of emulsifiers and fats and oils were presented as well as a method for their determination. Use of the method was illustrated by choosing an emulsifier combination for a typical cosmetic cream. The HLB system appears to be suitable for all types of problems employing surface-active agents.

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* NOTE: Span, Tween and Arlex are Reg. Trade Marks, Atlas Powder Company.