Relationship Among "Emulsion" Type, Detergency and Foam

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Abstract

Three test methods have been developed to show the measurably close relationship existing among detergency, foam, and the indication of the type of "emulsion" naturally inclined to form. Visual recognition of the state of the emulsion makes it possible to assess the system as to its comparative detergent capabilities and its foaming proclivities. Guided steps can then be taken for improvements. The methods have been used with success in formulating alkaline cleaning mixtures.

The first two methods relate emulsion type with wetting and detergency. They are used to show the effects upon that relationship of such factors as a) concentration of surfactant, b) concentration of added sodium chloride, c) temperature, and d) the nature of the oil.

It is pointed out that while the o/w emulsion conditions favor dishwashing, metal cleaning and bubble bathing, laundering would be favored by the w/o "system" where optimum conditions are to be found well-removed from the "inversion point."

The third method relates emulsion type with foam in an equally precise manner. The foam is produced by pouring intermittently. The tester for it is described more fully in a separate article (1). The role of foam in detergency is assessed. At the inversion point of the emulsion foam stability, not due to small bubble size, is at its greatest and, for example, so is the ease, speed, and completeness with which oily soils can be removed—a situation explaining hand dishwashing at its best.

Introduction

In earlier investigations no reliable correlation could be established between emulsions, detergency, or foam, and the results of measurements of any single fundamental physical property. In more recent studies on emulsions, however, Griffin (2), Becher (3) and Clayton (4) have been able to grade emulsifying agents in terms of their hydrophilic-lipophilic balance (HLB). That this method of classification is justified on a theoretical as well as on a practical basis where actual emulsions are concerned has been pointed out by Davies (5).

Ross et al. (6) have shown emulsion stability to be related to mutual spreading properties between the oil and water phases—another basic approach to problems in the detergent field. Becher (7) has called attention to the fact that spreading can be easily seen and could be used as a rapid index for the correct HLB for stability.

In the area of foam a great deal of research has been done to understand it better and to measure it. Of the many methods that have been proposed, the pouring method of Ross and Miles (8) has received the greatest acceptance, and not only in the United States by the American Society for Testing Materials (9) but recently by the French Detergency Committee (10) after a thorough screening.

In the field of detergency Goette (11) and Preston (12) and others to be mentioned later, have been able to show strikingly a relation with critical micelle concentration. Harwood (13), Mansfield (14), Stevenson and Adam (15) and Swanston and Palmer (16) have all emphasized the importance of emulsification, while Kling (17) emphasized wetting. In a comprehensive study of the effect of builders upon surface activity Harris (18) pointed out their effect upon surface and interfacial tension, wetting, detergency, and foam.

Another observation of interest to us in this present report is that of Greisinger and Nevison (19) who have reported that laboratory results from using a vegetable oil and mineral oil (and carbon) can be correlated with practical laundering results.

This recollection of progress made in the various areas of actual emulsions, detergency and foam is intended as background and additional justification for test methods and procedures about to be described. It is hoped the findings may be of use to those engaged more fundamentally in research in this general field and that "emulsion" type as we use it here may serve as sort of a common denominator for interrelating the separate physical properties.

When an emulsion is mentioned, one calls to mind an intimate mixture of at least two immiscible liquids such as oil and water, produced spontaneously or by vigorous mechanical means. One liquid—the dispersed phase—may be present in the form of droplets of microscopic size. The other liquid is regarded as the continuous phase.

In this paper we are linking detergency and foam with the state of an oil and water system that merely indicates its natural tendency to form an emulsion of one type or the other between a water solution of a surfactant or formulation and an oil to which nothing has been added previously. The oil at the outset of the two tests described here is allowed simple contact with the detergent solution, but it is otherwise undisturbed and undispersed in it. We have intentionally avoided the deliberate preparation of actual emulsions because, in their preparation, a number of factors become involved which tend to obscure the true inclinations of the systems.

As Davies (20) has put it, an emulsion consisting of 99% water phase and only 1% oil phase may by force become an oil in water (o/w) type despite a natural tendency to become a w/o type.

Most detergent work involving water and oil is concerned with a phase-volume ratio of this kind. It, therefore, becomes inadvisable to use persuasion on the system if its true character is to be ascertained. A preemptive masking of this character would also occur were the surfactant to be deliberately incorporated in the oil before testing.

Experimental

Materials

The tests made here involve various surfactants and proprietary formulations widely known for their domestic or industrial use. They are listed in Table I under their chemical names, along with percentages of active ingredients. In general, most of the unmentioned inactive component of the anionic surfactants consists of sulfate.

The oils used were either of vegetable origin, mineral, or animal, i.e., Wesson oil, Nujol, or lard. The lard had an acid value of 0.64, a fatty acid titer of

TABLE I

Surface-Active Materials Used

Surface-active material No.	Type	Chemical description	Active %
1	Anionic	Sodium laurate, Tech grade	Recrystallized
2	Anionic	Sodium lauryl sulfate	38.8
3	Anionic	Alkyl benzene sodium sulfonate	40
4	Anionic	Alkyl benzene sodium sulfonate	92
5	Anionic	Ammonium sulfate of mixed fatty acid monoglyceride	31
6	Anionic	Soap (60% on anhydrous basis) together with alkaline builders consisting of 0.9% chloride, 10.2% silicate of soda, and 7.8% tetrasodium pyrophosphate	76.9
7	Anionic	Sodium sulfate derivative of 3,9-diethyl tridecanol-6	25
8	Anionic	*Sulfonated castor oil*	50
9	Anionic	Sodium-N-methyl-N-oleoyltaurate	90
10	Anionic	Complex mixture of sulfonated ketones, amines, and alkyl sulfonates	35
11	Nonionic	Alkyl aryl polyethylene glycol ether	100
12	Nonionic	Ethylene oxide condensation product of a phenol	83
13	Cationic	Lauryl pyridinium chloride	80

37.8C, and a melting range of 27–45C, all of which characteristics are pertinent to its behavior under our experimental conditions.

Any builders used were inorganic electrolytes and, aside from sodium sulfate, consisted of sodium chloride, the alkali carbonates, silicates or phosphates.

Distilled water, deionized water, or tap water was used to prepare various aqueous solutions. The tap water was of moderate hardness, containing 109 ppm as $CaCO_3$.

Test I: Behavior of a Floating Drop of Oil

In this test the behavior of a sizable drop (0.4 ml) of oil is noted from all angles after it has been placed on the surface of an aqueous solution of a surface active agent, or formulation.

Equipment:

1—tall-form beaker, 60 mm diameter.

1—medicine dropper marked to deliver 0.4 ml.

1—water bath, transparent, glass, temperature-controlled. Water bath having a partial cover with suitable holes for suspending the beaker of aqueous solution and a test tube of the oil.

1 or more open-ended sheet-metal cylinders could be placed form-fittingly in the beaker were metal cleaning to be studied. The only requirement here is that a hole be cut in the metal wall at some place below the surface of the solution to permit viewing the drop of oil from below.

Procedure:

By means of a medicine dropper a globule of oil (0.4 ml) prewarmed to the desired temperature is placed near dead-center on the surface of the aqueous solution of surfactant, also prewarmed to the desired temperature.

The reason for adopting an oil drop of this large size is that it easily and visually shows by change in shape and behavior the effect of physical forces exerted upon it. Smaller drops, all the way down to microscopic size, such as those dispersed in an actual emulsion, would resist distortion to a much greater extent.

In this test, the transition form the o/w to the inversion point on the o/w side, and then to the w/o side is accompanied by a change in shape from a double convex lens to a sphere, and then to a doughnut shape. In this doughnut, the oil forms the ring and the water tends to force its way up through the center of the ring. It is by this phenomenon that we identify the true inclination of this so-called emulsion, regarding the system as of the w/o type.

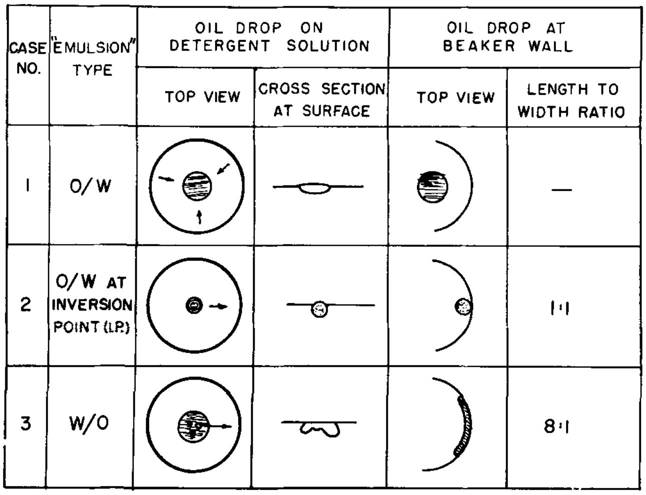

FIG. 1. Test I—behavior of drop of oil.

The evidence obtained relates not only to emulsion type, but also to wetting and to cleaning. This is illustrated in Figure 1. As in Case 1 of Figure 1, the o/w type of emulsion is indicated if the oil drop forms a lens convex to the solution, refuses to budge much from its centered position, or to gravitate toward the containing wall. This situation obviously favors dishwashing (or metal cleaning) inasmuch as the detergent solution preferentially wets the solid surface.

In Case 2 of Figure 1, the oil drop assumes a spherical shape, gravitates to the containing wall but makes contact with the wall at only one point. This situation describes the emulsion system as o/w at the inversion point (I.P.) and also favors dishwashing (or metal cleaning). The solution is still the preferential wetter of the containing wall.

In Case 3 of Figure 1, the drop becomes doughnut shaped, thinning in the middle, gravitates to the containing wall, and spreads along it. In Figure 1 we have indicated that the ratio of the spreading length to width may be taken as a rough measure of the extent to which the system has intruded the w/o system. Increases in this ratio from 1:1 up to 8:1 and beyond is a measure of the mounting tendency of the oil to preferentially wet the containing wall.

Obviously the purpose of dishwashing (or metal cleaning) would not be served by Case 3 except by attritional means; and except for a low ratio not much greater than 1:1, additional cleaning by rinsing would be difficult. That the situation given by Case 3 is better suited to laundering will be discussed further on. If, as it should be, the removal of oleophilic dirt (typified by carbon) is the criterion for laundering, then the oil being the effective outer phase will preferentially wet the dirt—a prerequisite in this cleaning operation.

Test I works well at room temperature when evaporation is slight. Evaporation induces a localized increase in concentration of the surface active agent at the surface, which causes a misleading shift in the general direction of the w/o configuration. To minimize the effect of evaporation when testing at higher temperatures, the aqueous solution should be stirred immediately before adding the oil, but gently enough to produce no foam. Then the measurements must be made quickly.

Test II: Time for Displacing Oil

In this test is measured the time taken for the initiation and completion of the displacement of oil from a small test tube submerged in an aqueous solution of surfactant. Cleaning effectiveness can be ascertained easily by visual means. Except for the benefits derived by determining the wetting ratio as in Test I, Test II tells the same story and affords additional information as to effectiveness and rate of otherwise unaided cleaning. Test II is independent of the effects of evaporation because the action takes place well below the surface of the otherwise undisturbed aqueous solution.

Equipment: See Figure 2a.

1 or more test tubes, glass, ordinary, 150 × 18 mm.

1 or more test tubes, glass or metal, 75 × 10 mm. *The diameter of these small test tubes is somewhat critical.* A fine wire is attached to the lip of each of these to aid in the test.

1—water bath, glass, transparent, temperature-controlled, and partially covered by sheet-copper. The larger tubes and contents may be hung in full view via suitable holes through the cover.

1—timer.

Procedure:

A number of the large and of the small test tubes are first cleaned thoroughly. The smaller ones may be oven-dried at 105C, but before they are used they should be covered from dust but otherwise exposed to consistent atmospheric conditions long enough for them to regain a normal amount of occluded moisture.

If, for example, the effect of concentration is to be studied, the number of large tubes are each in turn filled with aqueous solution of surfactant at a concentration increasingly different from its predecessor. They are then hung in the bath water and warmed to the desired temperature. A large test tube of the oil to be tested is also hung in the bath.

When the desired temperature is reached, a small test tube (75 × 10 mm) is filled to the brim with the warmed oil and gently lowered into the large test tube containing the lowest concentration of surfactant. The time is noted. The operation is repeated until all necessary concentrations are covered. Actually all that is needed is a minimum of two reasonable concentrations falling on the o/w side and two on the w/o side, wherever those might be.

The time for displacing the oil is then plotted against an independent variable, such as concentration, and illustrated by Figure 2b. The exact location of the inversion point is found at the intersection of the o/w and w/o curves.

If the oil and water system favors the o/w emulsion type, the time taken for the oil to be displaced may range from one minute to even one day, depending upon how far removed from the inversion point the system may be. For a system consisting of mineral oil (unsaponifiable) and distilled water, it might take a very long time in spite of the fact that the oil is less dense than the water.

If the o/w emulsion system is at the inversion point, ejection of the oil will be more or less immediate, perhaps in one minute or much less. If the w/o emulsion state is indicated the time for the ejection of oil will be immediate, a matter of seconds.

Figure 2c vividly illustrates the action for the respective situations just described. The situations for Case 1, Case 2, and Case 3 of Test II are respectively identical with those of Case 1, Case 2 and Case 3 of Test I. For the o/w situation of Case 1 of Test II (Fig. 2c), the oil remains undisturbed for a relatively long period of time, then begins to move out of the small test tube in comparatively large globules at first, followed by the complete ejection of the remaining oil, practically en masse. On the o/w side the globules would become smaller and smaller as the inversion point is approached. The test tube is left clean. The visual evidence is unmistakable. At the inversion point on the o/w side as shown by Case 2, the initiation of the action of ejecting the oil is almost immediate, and is completed rapidly. The oil rises in fine droplets, leaving the test tube clean. On the w/o side of the inversion point the action is immediate and completed quickly, the oil rising in a stream of emulsion. The tube is left still soiled with a film of oil, because the oil is the preferential wetter under these conditions.

Apart from its foam aspects, Case 1 should favor machine dishwashing where some mechanical effort would speed up cleaning. Case 2 should favor hand

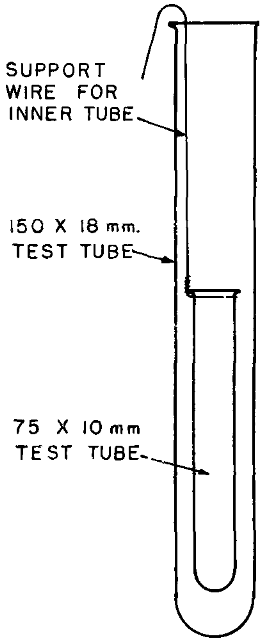

FIG. 2a. Test tubes for Test II.

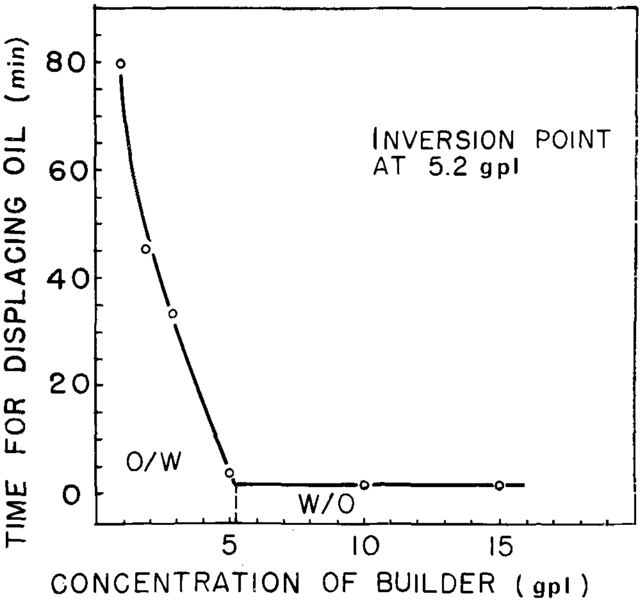

FIG. 2b. Graph exemplifying Test II.

TABLE II

Change of "Emulsion" Type with Change in Concentration of Surfactant in Distilled Water Solutions at 49C Against Mineral Oil

Anionic [a]		Nonionic [b]		Cationic [c]	
Concentration gpl	Emulsion type	Concentration gpl	Emulsion type	Concentration gpl	Emulsion type
0.15	o/w	0.096	o/w	1.29	o/w
0.31	o/w	0.15	near I.P.	3.23	o/w
0.50	o/w	0.192	w/o	6.45	o/w
0.60	o/w	0.384	w/o		
0.61	o/w	0.768	w/o		
0.62	near I.P.	1.23	w/o		
0.625	w/o	1.54	w/o		
1.0	w/o	7.68	w/o		
2.0	w/o				
5.0	w/o				

[a] Alkyl benzene sodium sulfonate (40% active).
[b] Ethylene oxide condensation product of a phenol (83% active).
[c] Lauryl pyridinium chloride (80% active).

dishwashing where complete oil removal should be carried out with the least effort. Case 3 is not suited to dishwashing or metal cleaning . True, Case 3 favors rapid removal of oil, but is bound to leave a film on dishes. Scott (21) has measured amounts of oils and fats remaining on cloth after laundering. The same reason that Case 3 leaves some oil on dishes must apply to cloth. Complete oil removal can only be brought about by attrition under these conditions. Perhaps a subsequent vigorous wash in a system such as Case 1 or Case 2 would favor complete removal of the oil from the cloth.

Effect of Concentration of Surfactant upon Emulsion Type

To show this effect, three surfactants were selected at random. One was anionic, one nonionic, and one cationic. They are listed in Table I as Surface Active Materials No. 3, 12 and 13, respectively.

Table II shows how the emulsion type as measured by Test II changes with the concentration of surfactant in aqueous solution against mineral oil when the temperature is held constant at 49C. Actually the concentrations were increased to only a practical limit. Table II shows that system containing this particular anionic passes through an inversion point at a concentration between 0.620 and 0.625 gpl; the particular nonionic at 0.15 gpl; and the cationic agent remains of the o/w type of emulsion without yet reaching any inversion point.

Effect of Concentration of NaCl upon Emulsion Type

Table III shows the effect of additions of sodium chloride, a builder with limited qualifications, upon emulsion type. The oil phase was lard, liquid at 49C. The data are illustrated by Figure 2b.

Effect of Temperature upon Emulsion Type

The effect of temperature upon emulsion type is just the opposite of the effect of such intensity factors as a) concentration of surfactant, and b) concentration of sodium chloride. Here, an increase in temperature tends to shift the system in the general direction of the o/w type.

TABLE III

Effect of Builder (NaCl) Concentration upon Type of "Emulsion" Naturally Tending to Form Between Lard and a Distilled Water Solution of an Anionic Surfactant at a Concentration of 0.5 gpl, and 49C (Surfactant, Alkyl Benzene Sodium Sulfonate, 40% Active)

NaCl gpl	"Emulsion" type
0	o/w
1	o/w
2	o/w
3	o/w
5.2	I.P.
10	w/o
15	w/o

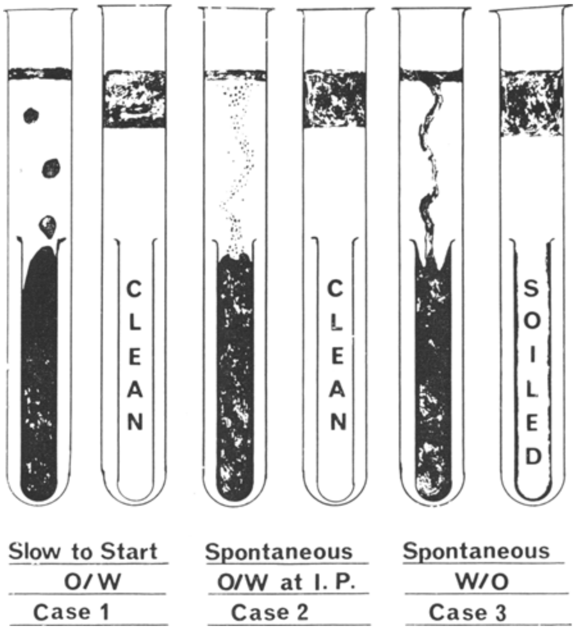

FIG. 2c. Emulsion tests by Test II.

This is all that Table IV is intended to show. Five sample formulations for hand dishwashing at 49C were prepared as tap water solutions at an arbitrary concentration of 2.5 gpl and submitted for rough screening by single observations under Test II. The formulations were alkaline in nature and composed of various amounts of alkyl benzene sodium sulfonate (40% active) and the silicates, the phosphates, and the carbonates of sodium. The tests were actually run at three different temperatures against Nujol (mineral oil) as well as Wesson Oil (vegetable), the latter serving more as a basis for judgment of the solutions for hand dishwashing restricted to 49C. Although only five formulations are listed, over one hundred were screened and found wanting.

Without delving into the merits of all of these five formulations it can be seen that at this arbitrary concentration of 2.5 gpl, Formulation X-4, being near the inversion point (I.P.) at 49C with both oils, easily satisfied hand dishwashing requirements. It was selected upon this basis, and has proved to be an excellent product.

Effect of the Nature of the Oil Upon Emulsion Type

According to Spring and Peale (22) the free fatty acid contents of certain oils have the effect to change the efficiency of removal of oily soils from steel. The results of Test II may shed some light upon this. The nature of the oil profoundly effects the concentration requirements of the various solutions to reach the inversion point of the emulsions.

Table V shows the concentrations of surfactants needed to reach the inversion points against Wesson

TABLE IV

Effect of Three Temperatures upon the Emulsion Type of 2.5 gpl Tap Water Solutions of Alkaline Formulations Against Vegetable and Mineral Oil

Formulation	25C		49C		71C	
	Wesson	Nujol	Wesson	Nujol	Wesson	Nujol
X-1	w/o	o/w	w/o	o/w	o/w	o/w
X-2	o/w	o/w	o/w	o/w	o/w	o/w
X-3	w/o	o/w	near I.P.	o/w	o/w	o/w
X-4	w/o	w/o	near I.P.	near I.P.	o/w	o/w
X-5	w/o	o/w	w/o	o/w	w/o	o/w

TABLE V

Concentrations of Various Surface Active Agents in Distilled Water Solution Needed to Reach the Inversion Point Against Vegetable Oil and Mineral Oil

Surface-active material from Table I (number)	Type	Temperature, C	vs. Wesson gpl	vs. Nujol gpl
2	Anionic	25	....	3.0
3	Anionic	49	1.5	0.6
4	Anionic	49	0.2[a]	..
5	Anionic	49	2.7	2.5
6	Anionic	25		1.0
7	Anionic	49	5.0	2.5
8	Anionic	49	>7	>7
9	Anionic	49	0.5	0.7
10	Anionic	49	4.0	10.0
11	Nonionic	49	5.5	0.6
12	Nonionic	49	1.5	0.1
13	Cationic	49	>7	>7

[a] Actually in presence of 6 ppm of hardness. See Figure 3.

oil (saponifiable) and against mineral oil (unsaponifiable). Griffin (23) recognizes this need to consider the nature of the oil for determining the HLB required for suitable actual emulsions.

Upon scanning the data of Table V one should be impressed by the wide divergence in the amount of surfactants required. For example, No. 12 needs an amount 15 times as great against Wesson oil as it does against mineral oil. No. 10 needed 100 times as much against mineral oil (Nujol) as does No. 12. While No. 12 against Wesson oil needs more than 7 times that for No. 4.

Although wide divergences do exist, caution should be used before jumping to conclusions. Reserve capacity may be a factor to reckon with in detergency and foam.

Emulsion Type and Laundering

At a point above the critical micelle concentration Preston (12) and Goette (11) noted a decided improvement in the laundering of textiles. Ginn and Harris (24) found that soil removal during laundering begins at the critical micelle concentration, but maximum detergency may occur at much higher concentrations, varying as much as 6 to 10 times the CMC for different surfactants.

We had wondered whether or not there might be a close relationship between CMC and the inversion point of our so-called emulsion. According to Long and Nutting (25), one of two closely agreeing values for the CMC of sodium laurate was 2.0×10^{-2} M at 25C. When we subjected water solutions of sodium laurate to Test II, the inversion point involving unsaponifiable mineral oil was reached at a concentration of 2.0×10^{-2} M. In this instance there is a close relationship. However, Table V generally shows that the nature of the oil may be a determining factor, and not CMC alone.

From the foregoing it can be concluded that good laundering will take place well into the region where the w/o type of emulsion obtains, somewhere near or beyond the ratio exemplified by Case 3 of Figure 1. Oil removal would be rapid but seldom complete. The criterion should be the removal of oleophilic dirt, typified by carbon, and facilitated by the suspending and dispersing power of the oil.

On the w/o side, the extent to which the oil functions as the continuous phase is only a matter of degree which is tempered by the unfavorable phase-volume situation usually obtained in laundering. Only when this handicap is sufficiently overcome, and the oil has a chance to make itself felt as if, in effect, it were the continuous phase, will good laundering be obtainable.

Table V shows wide variations in the amount of various detergents required to reach the inversion point. Because of this, it is conceivable that the effective concentration of a good detergent at which good laundering should take place could be a product of the concentration of the detergent needed to reach the inversion point times a simple factor greater than unity and reasonably common to all laundry detergents.

Emulsion Type and Foam

Dishwashing. When dishwater is suitable it is warm, foams easily, cleans and drains well, and is pleasant to touch. When not so warm, it feels greasy, the foam collapses, and the dishes emerge unclean. If one rewarms the dishwater without diluting it or without adding anything, it regains most of its original effectiveness even in the presence of accumulated oily soil.

Closer scrutiny would reveal that these changes are accompanied by an unobtrusive change in the type of emulsion merely tending to form. Upon cooling a little it shifts from o/w toward w/o.

In one special test to show the effect of water hardness upon emulsion type and foam stability, a 0.5 gpl solution of alkyl benzene sodium sulfonate (40% active), an anionic surfactant, was made up with tap water of hardness expressed as 109 ppm $CaCO_3$. A second solution at the same concentration (0.5 gpl) of the same anionic surfactant was made with distilled water.

The emulsion type with tap water solution was definitely w/o, and that with distilled water was o/w. As a parallel with actual emulsions, Bhatnagar (26) has established that multivalent metal ions such as calcium (hardness) have a much greater influence in causing inversion to the w/o type than have univalent ions such as the sodium in this anionic surfactant. The two solutions were separately used in hand dishwashing tests at 49C on dinner plates soiled with Wesson oil. Conclusions were based upon the number of plates that could be washed in a controlled manner before predeveloped foam was gone.

Under these conditions, the distilled water solution washed two plates. The tap water solution washed six. Upon the basis of our experience with emulsion type and an appreciation for the existence of maxima in detergency, it was predicted that the 0.5 gpl solution of the same surfactant as before, but made with one part tap water and three parts distilled water, would shift the system to near its inversion point. At that point foam, as we will prove further on, would have near-maximum stability.

The inversion point was approximated, the plates were washed, and a total of sixteen of them were made clean before the foam was gone.

Single Bubble Foam

In a second special experiment to show the effect of emulsion type upon foam stability, a Petri dish was partially filled with a 25C dilute aqueous solution of an anionic surfactant—alkyl benzene sodium sulfonate (40% active)—favoring the o/w type of emulsion with a drop (0.4 ml) of Wesson oil carefully placed on its surface with a medicine dropper as in Test I.

The oil drop became convex to the solution, approaching spherical shape signifying that it was in a state just short of that defined by Case 2 of Figure 1. The oil drop showed no inclination to gravitate toward the rim of the Petri dish, and gentle encouragement could not make it do so. These observations made it possible to identify this system as o/w, but near its inversion point.

By means of a Mohr pipette, dipping into the solution, a single but sizable bubble was carefully blown by mouth. It rose to the surface and reluctantly attached itself to the oil drop, but at a single point only. The bubble lasted a long time.

The foregoing experiment was repeated with a newly made solution of the same surfactant, but at a concentration high enough to favor the w/o system. After being blown, a newly formed bubble of a size equal to the first one rose to the surface and made immediate contact with a new drop (0.4 ml) of Wesson oil. This drop of Wesson oil presented itself concavely to the solution and was almost doughnut shaped as illustrated by Case 3 of Figure 1. Upon contact with the bubble the oil partially encircled it. The bubble broke immediately.

In the first instance, favoring o/w near the inversion point, the point of contact was a minimum and so, therefore, were the stresses upon the bubble.

In the second instance, favoring w/o, the extent of the contact of oil with bubble was considerably more, and so were the unbalanced stresses upon the bubble.

Continuing in its w/o character, the oil drop finally gravitated to the rim, made contact, and spread out alongside.

Agreement of Foam Test with Emulsion Test

In a third special experiment, the relationship between emulsion type and foam is shown in a very striking and quantitative manner.

In this experiment at 49C the concentration of surfactant remained constant throughout the interrelated foam tests and the emulsion tests by Test II. The solutions for the emulsion tests were prepared by the same person who carried out the tests. Separate solutions for the foam test were prepared a week later by another person who then performed the foam tests.

The foam tester, Test III, is more fully described in a separate article, (1). The foam was developed by pouring, the action being intermittent. The belief that this method has basic attributes is confirmed by the results of this third special test.

In this third special test at 49C the concentration of alkyl benzene sodium sulfonate (No. 4 of Table 1, 92% active) was fixed throughout at 0.2 gpl. A 0.2 gpl solution in deionized water was first prepared. A second solution containing 0.2 gpl of the surfactant was also prepared, but from tap water having a hardness of 109 ppm as $CaCO_3$. The two solutions were mixed in varying proportions to give solutions of increasing percentages of tap water.

By Test II the time taken for each of the prepared mixtures to displace Wesson oil from the 75 × 10 mm test tubes was measured. Displacement times as ordinate were plotted against percentages of tap water in a manner similar to that illustrated by Figure 2b.

On the basis of our experience with emulsion type it was predicted that maximum foam stability would occur at the tap water concentration of 6% established by Test II as the inversion point.

As shown by Figure 3, the foam stability (or volume, here) reaches a maximum at about 8% tap water—a disagreement corresponding to a difference of only 2 ppm of hardness as $CaCO_3$.

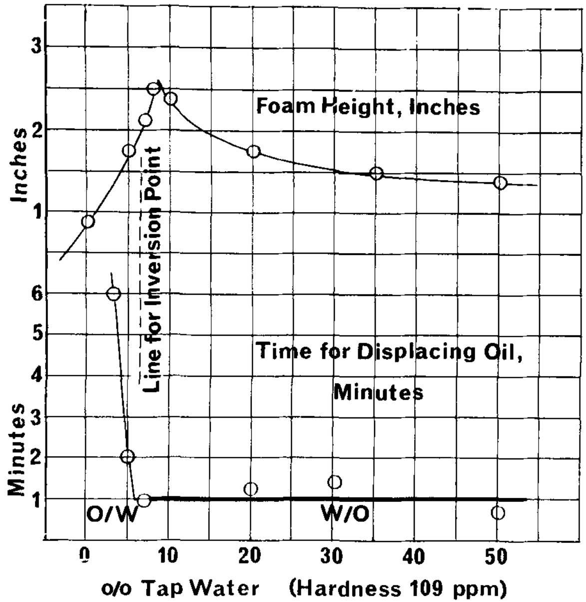

FIG. 3. Relationship between "emulsion" type and foam.

The Role of Foam

While foam stability serves as an index for good hand-dishwashing, high foam volume and long-lasting small bubbles do not so serve because these can result from relatively high effective concentration of detergent, as normally characterized by the w/o configuration.

As has been said, the optimum conditions for laundering should be found at detergent concentrations well above the CMC and intruding well into the w/o emulsion area. If we start with this situation and develop considerable foam by vigorous agitation of the solution, the net result will be a lowering of the concentration of the surfactant in the body of the solution and a consequent shift from the favorable w/o situation in the general direction of the o/w situation. Ability to remove oil completely will increase, but ability to suspend, disperse, and remove oleophilic dirt will decrease.

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