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Disposition of Soap in Detergent Operations

by E. W. COLT and C. V. SNELL
ARMOUR & CO., 31ST ST. AUXILIARIES, CHICAGO, ILL.

DETERGENT operations usually involve the presence of fabrics, soil in intimate contact with the fabrics, and water containing more or less hardness in the form of calcium and magnesium salts. The object of the operation, of course, is to remove the soil from the fabric and to maintain the soil in a state of deflocculation. In accomplishing this result there are four principal dispositions made of the soap. A portion of the soap is used in satisfying the demands of the calcium and magnesium ions present. A second portion of the soap is adsorbed from the solution by the fabric. The soil removed from the fabric during the detergent operation requires a third portion of the soap to effect deflocculation, and finally, a definite effective concentration of soap solution must remain after satisfying the three forementioned demands to provide the desired degree of lathering power and detergency, this concentration being determined by the composition of the soap and the temperature of the detergent operation.

When suds and detergency tests are determined as a function of the concentration of the soap solution, a suds or a detergency curve is obtained that has the characteristics of Figure I. A certain minimum value of the concentration is necessary before sudsing action appears and there is a maximum concentration beyond which improvement in sudsing action does not result; similarly with the detergency curve but the location of the curve along the concentration axis does not necessarily correspond to the location of the curve for the sudsing action. The position of the two curves shifts to the left or right along the concentration axis depending on such factors as the fatty acid composition of the soap, the amount and nature of alkaline builders, the degree of hardness of the water, the temperature of the solution, the kind and amount of the fabric load, and the kind and amount of soil present. The interesting point is that each combination of conditions results in a fairly definite concentration at which sudsing action and detergent action become effective. The minimum concentration at which good detergency is obtained in the absence of water hardness, fabric load, and soil load, may be considered the effective concentration mentioned earlier as being required to produce adequate detergency after satisfying the other three factors.

Attention has been called to the fact that the fabric load affects the concentration required to produce satisfactory sudsing and detergent properties. This fact has been studied by Neville & Harris (1) and by Williams, Brown and Oakley (2) who noted that fabrics selectively adsorb alkali in greater degree than the fatty acid. Acharya and Wheeler (3) expressed their belief that an association exists between adsorption and cleansing power. Adams (4) showed that the amount adsorbed varies considerably with the different detergents and that this adsorption is sufficient to reduce the effective concentration of the detergent. If fabrics adsorb alkali to an extent in excess of the fatty acid radical, as stated by Williams and others, it follows that definite disturbances must result in the nature of the soap remaining in solution. Investigators which include McBain (5, 6, 7, 8, 9) Hartley (10), Rebinder and Petrova (11), McBain & Salmon

(12), Nickerson and Serex (13), Vincent (14) have dealt with the nature of the soap solutions and briefly the composite view appears to be that in concentrated solutions, the soap may be predominately undissociated colloid micelle, at somewhat lower concentrations the colloidal ion or ionic micelle becomes more conspicuous and at still lower concentrations the crystalloid form predominates, both as undissociated crystalloid and ionized crystalloid, and finally at the low concentrations, hydrolysis of the soap becomes more pronounced and acid soap is formed. Under any set of conditions equilibrium between these constituents results.

Disagreement arises over which state affords best sudsing and detergent qualities. In 1922 McBain (5) stated that acid soaps exhibit no surface activity and detergent action is due mainly to undecomposed soap. Chapin (15) found that the hydrolyzed portion of soap is not only ineffective as a deflocculent but also inactivates an additional portion of unhydrolyzed soap which is necessary to deflocculate the free fatty acid produced. On the other hand, Levitt (16) considers the presence of acid soap an aid in detergency while Vincent (14) suggests that the soap concentration which produces the strongest selective adsorption of positive ions will give the optimum stabilization. Neville and Harris (1) offer data indicating that the principal surface-active constituent of a soap solution, to which is attributed its efficiency as a detergent, is the acid soap. Nickerson and Serex (13) also conclude that the surface activity of soap is determined to a great extent by the acid soap.

The subject of soap adsorption by fabrics and its effect upon the soap remaining in solution appeared to warrant further investigation. Many of the results by previous investigators were obtained with no consideration being given to the concentrations at which soap is normally found to be most effective as a detergent. The present work was undertaken with the view of perhaps learning somewhat more about these controversial points. In the tests which follow, except where otherwise stated, the soap used consisted of the sodium salt of an 80% tallow-20% coconut oil mixture. To avoid repetition, all adsorption tests were performed with a load to solution ratio of 1:10, the load consisting of cotton sheeting, and at a temperature of 43.3° C. (110° F.) except where otherwise stated. The tests were performed in distilled water free from CO_2. Solutions containing the fabrics were agitated for one hour which was found to be sufficient time to establish equilibrium. The adsorption effect was determined by noting the change that had occurred in the concentration of the solution at the conclusion of the experiment. In those experiments in which the detergent was entirely soap, the concentration was determined by evaporating 250 ml. of the solution to dryness. Where the detergent comprised a mixture of soap and alkaline salt, the concentration of the total detergent present in the solution at the conclusion of the test was determined by evaporating to dryness. The soap content was then determined by extracting this residue with alcohol and evaporating the alcohol-extract to dryness. The alkaline salt content of the solution was determined by difference. The adsorption by the fabric was then computed from the data so obtained. All pH determinations were made with the hydrogen electrode.

Table I shows adsorption data obtained with cotton, rayon, silk, and wool. The larger value for wool is in accord with the findings of previous investigators. Figure II shows the adsorption of soap by cotton as a function of the initial concentration of the soap solution. The percentage adsorption of the soap from solution is somewhat greater at lower concentrations than at higher concentrations which is as should be expected. Figure III shows adsorption as a function of temperature. It is interesting to speculate on the significance of the maximum adsorption occurring at about 55° C. (130° F.). The authors can suggest no explanation except that it is undoubtedly related to the forms of soap in equilibrium at the particular temperature.

TABLE I

PERCENTAGE ADSORPTION OF SOAP FROM 0.100% SOAP SOLUTION BY VARIOUS TEXTILE FIBERS.

Fiber	Percent Adsorption
Cotton	19.5
Rayon	7.6
Silk	11.1
Wool	60.0

In the foregoing tests selective adsorption of alkali, as evidenced by a lowering of the pH values of the solution, was observed. This would appear to confirm previous assertions that preferential alkali adsorption by fabrics does occur. However, in de-

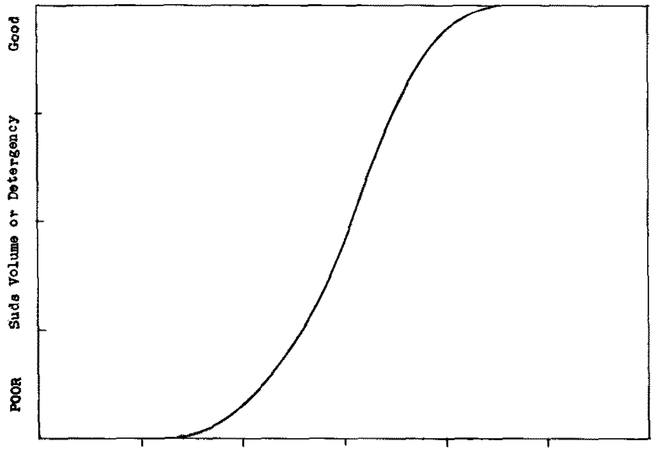

FIGURE I

Characteristic Relation between Suds Volume or Detergency and Concentration of Soap Solution.

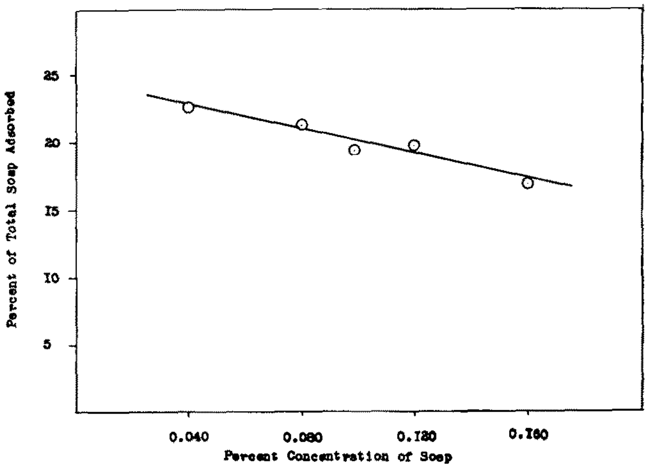

FIGURE II

Adsorption of Soap by Cotton, as a Function of the Initial Concentration of the Soap.

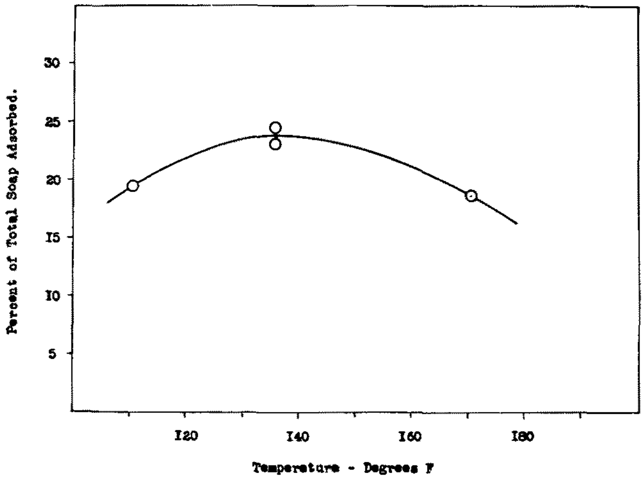

FIGURE III

Adsorption of Soap by Cotton, as a Function of Temperature.

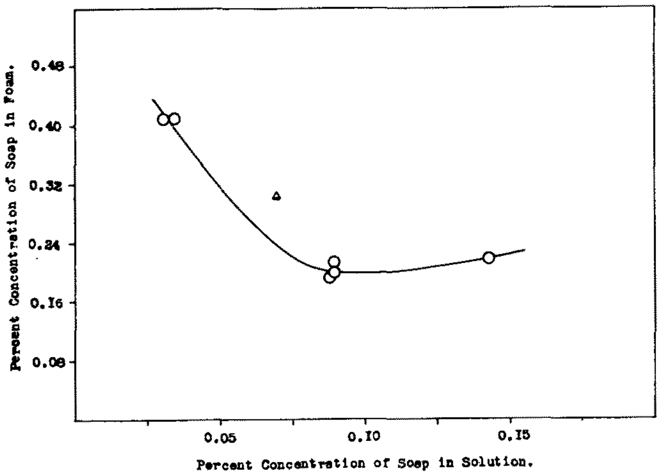

FIGURE IV

Relation of Concentration of Soap in the Foam to the Concentration of Soap in the Solution with which it is in Equilibrium.

termining the adsorption of the salts of pure fatty acids by cotton fabric, it was observed that a greater differential between the original and final pH values of the solution occurred in the case of sodium laurate (C_{12}) than in the case of the soaps of the longer carbon-chain acids. When these solutions were titrated back to their original pH value, it was found that less alkali was required to restore the sodium laurate to its original pH than to restore the soaps with longer carbon-chain length to their original pH values. The higher alkali adsorption from the soaps of the longer chain length acids was to be expected since it is known that hydrolysis increases with the length of the carbon chain. The drop in pH value in the case of sodium laurate seemed to offer one plausible explanation and that was that CO_2 absorption from the air was occurring and was having the greatest effect on the pH of sodium laurate which afforded the least buffering action at that pH range.

To determine what effect the normal CO_2 content in the air might have on the pH of soap solutions, air was passed through caustic soda solution to remove CO_2, then through water to saturate the air with water vapor, and then bubbled through 150 ml. of an 0.100% soap solution. The air, together with the foam that was formed, passed into a flask in which the foam remained and from which the air was allowed to vent. Approximately equivalent volumes of air were used in each experiment. pH determinations and the concentration of soap in solution and in the foam were determined at the end of each test. A similar test was conducted with air which had not been scrubbed to remove CO_2. The data, shown in Table II, reveals that when CO_2 was present in the air, the pH value of the foam but not of the solution was diminished. When no CO_2 was present in the air, no change in pH occured, either in the solution proper or in the foam. When the foam was evaporated down to dryness at 110° C., and redissolved in CO_2-free distilled water to the same concentration, the same pH as was obtained on the original solution, was observed. It might appear that if hydrolysis did occur, the resulting sodium carbonate and acid soap must have remained co-existant in the foam.

To determine just what effect a fabric load would have, a similar experiment was performed with 15 grams (1 :10 load ratio) of cotton sheeting using CO_2-free air. The results are shown in the third column of Table II. It is interesting to note that in this case the pH value was lowered in both the solution proper and the interface or foam, indicating that not only did hydrolysis occur, as of course was to be expected from the results earlier obtained, but that the distribution of acid soap between the solution proper and the interface appeared to be equitable. In this particular case CO_2, and thus sodium carbonate, was not a factor. Upon evaporating the foam to dryness and redissolving, no change in pH value occurred. Furthermore the solution was cloudy, all of which would indicate the presence of acid soap.

TABLE II

EFFECT OF PASSING AIR THRU 0.100% CONCENTRATION OF SOAP SOLUTION

	1 Air Free From CO_2	2 Normal Air Containing CO_2	3 CO_2-Free Air Plus Cotton
Initial pH of Solution	10.00	10.00	10.00
Final pH of Solution	10.00	9.95	9.50
pH of Suds Formed	10.00	9.00	9.50
Weight of Foam	13.4 grs.	16.4 grs.	8.89 grs.
Concentration of Soap in Foam	0.202%	0.195%	0.304%
Final Concentration of *Soap in Solution*	0.090%	0.088%	0.070%

These observations are not in agreement with experimental results obtained by Neville and Harris (1) who found that the foam formed by passing CO_2-free air through a soap solution was less alkaline and the final solution-proper more alkaline than the original soap solution. In other words, they found that acid soap accumulated in the interface. Possibly the difference between these two sets of observations may be attributed to the fact that Neville and Harris used a pure olive oil soap or essentially sodium oleate whereas the present work was performed with a tallow-coconut oil soap containing the soaps of short chain acids as well as long chain acids.

Similar experiments were performed on various concentrations of soap solutions and the equilibrium between solution concentration and interface concentration determined. The results are indicated graphically in Figure IV. The concentration of soap in the foam was not only greater than in the solution, as was of course to be expected, but the concentration of

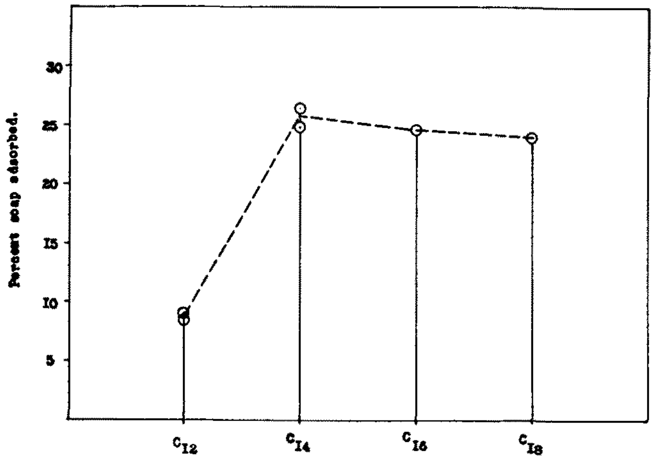

FIGURE V

Adsorption of Soap by Cotton as related to the Carbon Chain Length of the Pure Single-Component Soap.

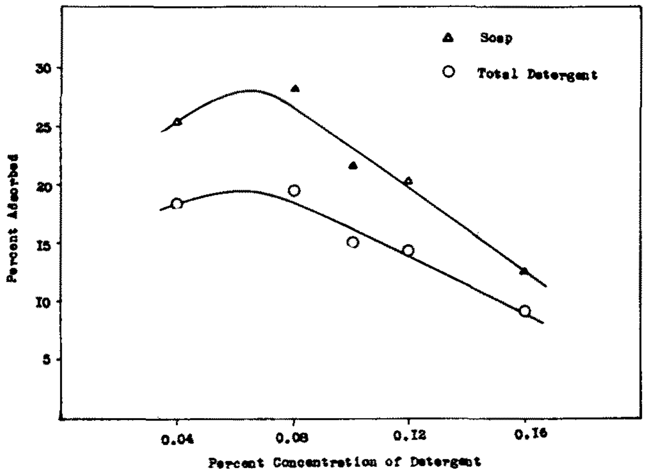

FIGURE VI

Adsorption of Soap by Cotton from a Detergent Solution Containing 70% Soap-30% Sodium Carbonate, as a Function of Concentration of Detergent

soap in the interface was actually greater in equilibrium with the more dilute solutions than when in equilibrium with the more concentrated solutions. Two explanations seem possible. At the lower concentration of soap solutions hydrolysis occurs to a greater degree. Acid soap is thus formed which, due to its greater surface activity, might presumably result in a higher concentration of soap in the interface. The equilibrium between soap in actual solution and soap in the interface was calculated from the data in Table II, column 3, in which selective adsorption of alkali by cotton fabric occurred and acid soap thus formed. Correction was made for the soap adsorbed by the cotton by using the information in Figure II which shows the adsorption of soap by cotton as a function of the concentration of the solution. The point obtained by this calculation is indicated in Figure IV by a triangle and it will be noted that the concentration of soap in the interface is appreciably in excess of the value to be anticipated from the curve which thus tends to support the proposed explanation.

However, it seems more likely that the increase in soap concentration in the interface at low concentrations of solution may have another and better explanation. The soap used in these experiments, as previously stated, was made from 80% tallow-20% coconut oil. The fatty acid composition, therefore, includes acids from caproic, (C_6) up to and including stearic (C_{18}). Suds tests performed in this laboratory but not included in this paper revealed that sodium laurate requires a concentration of 0.14% to yield the same foaming power as can be obtained from sodium palmitate at 0.06%. Consequently, it is reasonable to assume that agitation of a low concentration of a tallow-coconut oil soap would result in a selective suds formation containing the soaps of the longer chain-length acids and that agitation of higher concentrations would result in a less selective foam formation. Since sodium palmitate is a far better detergent than sodium laurate, the tendency for the former to produce a more concentrated foam would seem logical.

The effect of the carbon-chain length of the fatty acid radical on the adsorption of the soap by cotton was determined. Results are for saturated acids only and are presented in Figure V. The adsorption of sodium laurate was only one-third that of the C_{14}, C_{16}, and C_{18} soaps. In addition, it was found that sodium oleate gave an adsorption value of 17.8% while sodium resinate showed 18.5%. It may be significant that sodium laurate is a poor detergent, even at concentrations high enough to produce an abundant foam, whereas sodium myristate, palmitate and stearate, are by comparison effective detergents. The lower adsorption obtained in the case of sodium laurate may be explainable on the basis of less hydrolysis and hence less acid soap formation, in which case it might be expected that the addition of an alkaline salt to sodium palmitate should reduce the extent of soap adsorption by fabric.

The discussion up to this point has considered soaps unassisted by alkaline builders. The opinion prevails that the addition of alkalies to soap invariably effect an improvement in the detergent properties of the soap. In fact, many investigators contend that the addition of an alkaline salt to a soap solution beneficially suppresses hydrolysis or beneficially induces micelle formation. Neville & Harris (1) however, express an opposite view. They point out that the addition of alkali to a neutral soap raises the surface tension by suppressing hydrolysis and decreases effectiveness of soap as a detergent. No one appears to have considered whether the presence of an alkaline salt would suppress the adsorption of soap by fabric and whether if such suppression (or perhaps selective adsorption of alkaline salt) did occur, it was beneficial or objectionable from a detergent standpoint.

Adsorption studies were consequently conducted on several alkaline salts added to a soap solution. Table III shows the values obtained. The first column indicates the total detergent adsorbed expressed against the initial concentration of the detergent mixture. The second column indicates the actual soap adsorbed expressed against the initial concentration of actual soap. In no case did adsorption of alkaline salt by the fabric occur. Nor did the presence of alkaline salts exhibit any tendency to suppress the adsorption of soap by fabric. This might be taken to mean that hydrolysis with consequent acid-soap formation is not a conspicuous factor in adsorption of soap by fabrics. However, it is doubtful whether this conclusion is true

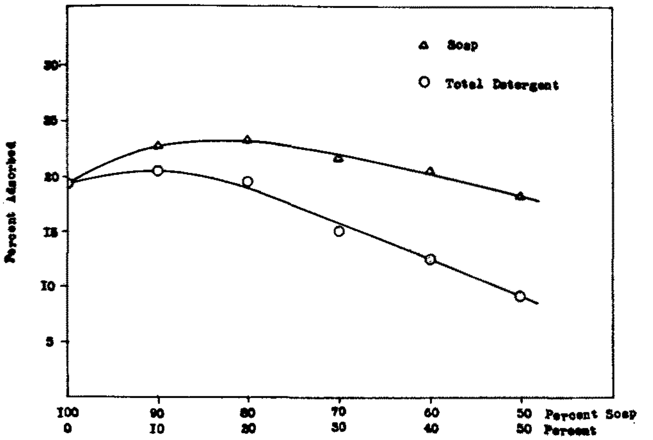

FIGURE VII

Adsorption by Cotton from 0.100% Solutions of Detergent Comprising Varying Percentages of Soap and Sodium Carbonate.

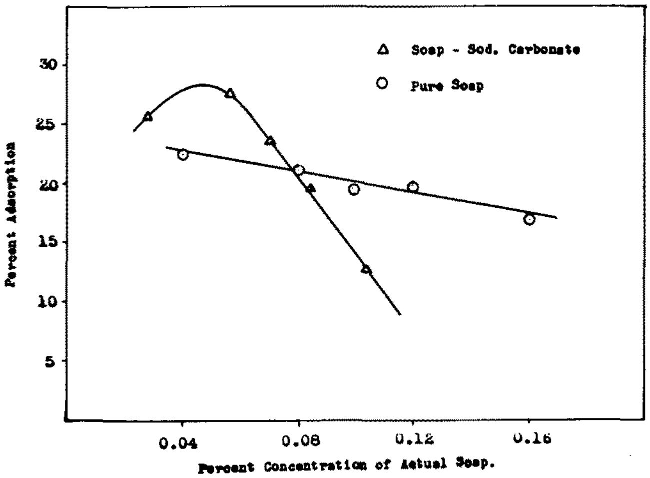

FIGURE VIII

Comparison of Adsorption of Soap from Pure Soap Solution and from a 70% Soap-30% Sodium Carbonate Solution, Basis the Actual Soap content of the Solution.

in view of the observations that follow. The adsorption of a detergent comprising 70% soap, 30% sodium carbonate by fabric was determined as a function of the initial concentration of the solution. The data is indicated in Figure VI. As in the pervious series, no adsorpton of soda ash by fabric was observed at any concentration of the solution. A maximum adsorption of soap expressed against the amount of soap in solution occurred at a concentration of about 0.08% and above this value the adsorption of soap fell off rapidly.

TABLE III

ADSORPTION OF SOAP BY COTTON FROM A SOLUTION OF DETERGENT COMPRISING 70% SOAP-30% ALKALINE SALT

Solution	Percentage of Total Detergent Adsorbed	Percentage of Initial Soap Adsorbed	Percentage of Initial Alkaline Salt Adsorbed
0.07% Soap	21.2	21.2	—
0.07% Soap plus 0.03% T.S.P.	15.0	21.4	nil
0.07% Soap plus 0.03% Sod. Carb.	15.0	21.8	nil
0.07% Soap plus 0.03% Tetra Sod. Pyrophos.	15.5	22.3	nil
0.07% Soap plus 0.03% Buffered Sod. Hexameta Phos.	16.1	23.0	nil
0.07% Soap plus 0.03% Sod. Sil. — N	16.8	23.8	nil
0.07% Soap plus 0.03% Neutral Soda	16.6	24.0	nil
0.07% Soap plus 0.03% Sod. Meta. Sil.	17.0	24.4	nil

Again considering the effect of sodium carbonate on soap adsorption, various ratios of soap to soduim carbonate were studied at a fixed concentration of 0.100% total detergent and the results are indicated in Figure VII. These data indicates that at this particular concentration of total detergent, the addition of 20% of sodium carbonate to the detergent formula causes an increase in the adsorption of soap by fabric as compared to the adsorption occurring with pure soap. Higher ratios of sodium carbonate to soap result in a gradual diminution in the amount of soap adsorbed. Since an increase in the sodium carbonate to soap ratio in this series results in a reduction in the actual soap concentration in the solution, this tendency downward is just the reverse of what occurs on decreasing the concentration of soap in the absence of sodium carbonate (See Figure II).

The data shown in Figure VI has been recalculated to show the relation between the percent of the total actual soap adsorbed by the fabric and the percent concentration of actual soap in solution disregarding the sodium carbonate. On the same chart (Figure VIII) is super-imposed Figure II which shows the same comparison for pure soap. The same treatment was accorded the data from Figure VII and the results are shown in Figure IX. In Figure VIII the ratio of soap to sodium carbonate, was the same for all points on the curve, *namely*, 7:3. The corresponding curve in Figure IX, however, has a varying ratio of soap to sodium carbonate, the ratio being low at the lower concentration of actual soap and approaching infinity at 0.100% concentration of actual soap. Considering Figures VIII and IX collectively, it is found that: —

At 0.04% concentration of actual soap:

> The presence of 30% sodium carbonate in the detergent formula *increases* the percent of actual soap adsorbed, compared to pure soap.

At 0.04% concentration of actual soap:

> The presence of 60% sodium carbonate in the detergent formula *decreases* the percent of actual soap adsorbed, compared to pure soap.

At 0.08% concentration of actual soap:

> The presence of 30% sodium carbonate in the detergent formula has *no effect* on the percent of actual soap adsorbed.
>
> The presence of 20% sodium carbonate in the detergent formula *increases* the percent of actual soap adsorbed.

At 0.12% concentration of actual soap:

> The presence of 30% sodium carbonate in the detergent *decreases* the percent of actual soap adsorbed.

This is graphically represented in Figure X. The curve represents an approximate boundary at which sodium carbonate has no effect on the adsorption of soap. Higher concentrations of sodium carbonate decrease adsorption while lower concentrations increase adsorption. This relation, of course, holds only for the condition of the experiment, i.e. a temperature of 110° F. no calcium or magnesium salts present, an 80-20 tallow-coconut oil soap, and a load to solution ratio of 1:10 the load comprising cotton fabric.

The significance of this behavior appears to be that at low concentration, where hydrolysis would normally be considerable, the addition of alkali first decreases

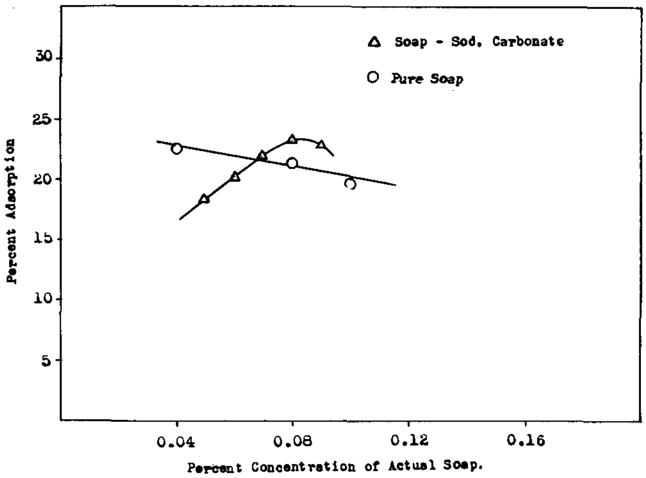

FIGURE IX

Comparison of the Adsorption of Soap from Pure Soap Solution and from Varying Percentages of Soap to Sodium Carbonate Solutions, Basis the Actual Soap Content of the Solution.

hydrolysis but upon further addition promotes micelle formation, the maximum adsorption occurring at some intermediate stage probably rich in crystalloid. At high concentrations where hydrolysis would appear to be less pronounced, the addition of sodium carbonate even in small amounts increases micelle formation and thus lowers the percent soap adsorption by fabrics.

In view of this analysis it would appear that the data in Table III should not be considered as indicating no appreciable effect by nor differences between various alkaline builders on the adsorption of soap by fabrics since the concentration of these tests by chance happened to fall close to the intersection of the adsorption curves for pure soap and for 70% soap plus 30% sodium carbonate. Presumably, all of the alkalies may be expected to show effects similar to sodium carbonate but quite possibly in different degrees.

The thought was previously expressed that additions of alkali to soap was generally considered to have beneficial effects on the detergent qualities of the soap. In standardized detergent tests, as run in this laboratory, detergent results on the standardized specimen of soiled textile fibre were rated numerically by visual methods from 1.0 to 5.0, the lower number representing perfect detergency and the higher number, no detergency. When the washing test was performed at 0.08% concentration of pure soap in the absence of a fabric load other than the test specimen which was negligible as a load factor, a detergent rating of 1.0 was obtained. When sodium carbonate was added to the extent of 0.035% in addition to the 0.08% of soap, a detergent rating of 2.0 resulted. That is, in the absence of a load the addition of sodium carbonate did not assist but actually hindered the detergent action of the soap. When the same experiments were performed with a load of clean cotton towels (load to solution ratio of 1:10) a detergent rating of 4.5 was obtained when sodium carbonate was absent and 3.0 when sodium carbonate was present. The poor detergency when a load was employed was due to the adsorption of soap by the load which diminished the effective concentration of the soap. But whereas sodium carbonate was objectionable in the absence of a load it was beneficial when a load was present. The

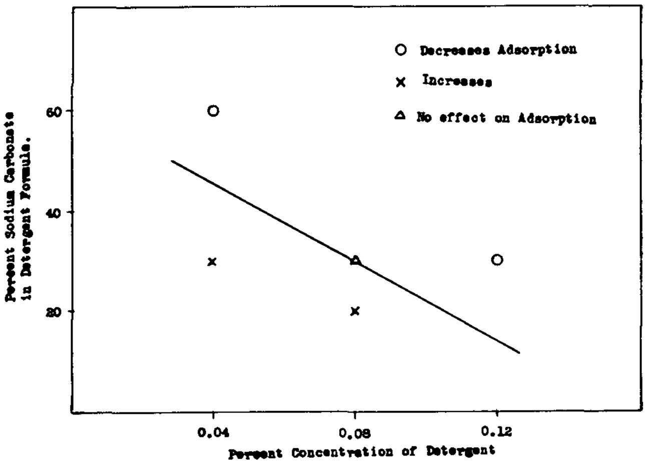

FIGURE X

Effect of Sodium Carbonate on the Adsorption of Soap by Cotton.

pH determinations on the soap solutions at the beginning and at the end of the tests indicate what presumably occurred. While no load was present there was a drop of 0.4 pH between the start and the finish of the test, both with pure soap and with soap to which sodium carbonate had been added. When a fabric load was present, pure soap resulted in a drop of 1.5 pH between the start and finish of the test, whereas soap plus sodium carbonate showed only a drop of 0.4 pH between start and finish. At the particular concentration employed, the addition of sodium carbonate to soap neither increases nor decreases the extent of soap adsorption by a 1:10 load of cotton.

Since in the absence of a load factor, there is less tendency for acid soap to form, the fact that additions of carbonate in increasing amounts to a fixed concentration of soap impairs the detergency of the soap, would indicate that the effect of the addition of sodium carbonate must be due, not to the prevention of hydrolysis, but to the shifting of the form of the soap in the direction of undissociated crystalloid or to the micelle form, but since the presence of a fabric load results in selective adsorption of alkali in amounts greater than the adsorption of fatty acid radicals, and detergency in the presence of a substantial load is benefited by the presence of sodium carbonate, the indications would be that acid soap, in substantial amounts at least, is objectionable. These two observations seem to indicate that the most effective form of soap is crystalloid.

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