The Deposition of Lime Soap on Fabrics During Washing

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ONE of the important disadvantages of soap as a detergent or textile assistant in hard water is that insoluble calcium and magnesium soaps tend to deposit on the material being treated. Much attention has been given to minimizing this effect by adding to the soap bath various synthetic detergents which, when used for this purpose, are loosely referred to as lime soap "dispersers" or "protective agents." Synthetic detergents differ quite widely in their ability to peptize an aqueous suspension of lime soap curd, and conversely in their ability to prevent the agglomeration or clotting of lime soap which is formed in their presence. It has generally been assumed that those surfactants which are the best peptizing agents for lime soap will be most effective in preventing its deposition on fabrics during washing. The tests most widely used to estimate the lime soap dispersing power of a surfactant are essentially measurements of the minimum quantity and concentration of the surfactant necessary to peptize lime soap (1, 2).

There have been few, if any, attempts to estimate directly the amount of lime soap deposited on fabric or the extent to which this deposition may be influenced by the presence of protective agents. It is obvious and easily demonstrable that agglomerated clots of lime soap can be transferred from the bath to the fabric by a purely mechanical filtering action whereas peptized lime soap cannot be filtered out in this manner. There is, however, so far as we are aware, no basis for predicting to what extent the lime soap, either clotted or peptized, will be held firmly to the fabric by adsorption or adhesion forces. We shall, for purposes of convenience, refer to a deposit not easily removed by rinsing as a firm deposit.

A primary purpose of this investigation was to explore the phenomenon of lime soap deposition on fabrics during washing. In order to do this it was first necessary to develop a suitably accurate and rapid method for determining the lime soap content of fabric swatches. The present paper describes the method and some of the effects which have been clarified through its use.

Experimental Methods

Preparation of Fabrics. The Tergotometer was used as the instrument for washing, and Indian Head cotton (Nashua Mfg. Co.) as the fabric. The fabric was used as received from the mill without rinsing or soiling. All washings and rinsings were carried out at 120°F. with the Tergotometer running at 100 oscillations per minute. The hard water was prepared by adding $CaCl_2$ and $MgCl_2 \cdot 6H_2O$ to distilled water in such proportion that the ratio of calcium to magnesium, calculated on a molecular equivalent basis, was 3 to 1. All hard water baths and rinses contained 360 ppm. hardness calculated as $CaCO_3$.

A standard cycle included one washing operation and two rinsing operations, as follows: One liter of the washing bath was made up and brought to temperature. Thirty-three g. of fabric (in the form of 5 swatches approximately 6½ inches square) were introduced and washed for 3 minutes. The fabric was removed and passed through squeeze rolls so adjusted that the damp fabric after squeezing weighed 66 g. (100% pick-up). The fabric was then run in one liter of rinsing water for 3 minutes and again removed and squeezed to 100% pick-up. A second similar rinse was applied, and after the final squeeze the fabric was oven-dried at 70°C. In order to obtain realistic quantities of lime soap on the fabric it was subjected to 10 such cycles, except where the data specifically indicates otherwise.

Analysis for Lime Soap. The analytical procedure consists of a direct non-aqueous titration of the fabric (or the fabric extract) with perchloric acid. It is essentially an adaptation of the titration procedures described by Palit (3). The solvent used was a mixture of equal volumes of ethylene glycol and n-butanol. This solvent was found to dissolve calcium and magnesium soaps quite rapidly at temperatures above about 70°C. and to hold them in solution on cooling. The perchloric acid was made up and standardized to .05 normal in the same solvent. Using reagent grade 72% perchloric acid, the amount of water in the final standard acid solution is harmlessly small. The most effective indicator was found to be methyl purple, manufactured by the Fleisher Chemical Company of Washington, D. C. Methyl red could also be used, but the end points were not as sharp as might be desired.

Two different titrating procedures were used. In the first procedure approximately 5 g. of the fabric, conditioned at standard temperature and humidity, is accurately weighed and placed in 75 ml. of solvent. The mixture is warmed to about 70°C. for 15 minutes with intermittent shaking. It is cooled slightly and titrated with the standard acid, using 8 to 10 drops of indicator. On re-warming and shaking, a permanent end-point is reached. Since the end point becomes diffuse when lower concentrations of perchloric acid are used, it is necessary to use a microburet. The amount of acid required in the above procedure was in every case less than 10 ml. In this procedure a blank determination should also be made with the original clean fabric. Perchloric acid in this solvent will titrate strong bases and salts of strong bases with weak acids. It will thus titrate Ca and Mg soaps, residual Na soaps, and any basic ash which may be found in the fabric. It will not titrate $CaCl_2$, $CaSO_4$, salts of the common sulfated and sulfonated detergents, or salts of other strong acids. An appreciable blank value is obtained with the original fabric. This is ascribed primarily to the ash content and secondarily to adsorbed soap from the mill processing. There is also a small indicator blank. The above procedure is useful in ascertaining the degree to which lime soap deposits are localized since the sample can be cut from any portion or portions of the washed fabric. It is disadvantageous because the presence of the fabric obscures the end point, introduces a blank value, and necessitates re-warming and shaking in order to attain a permanent end point.

In the alternate procedure, designed to eliminate the above disadvantages as well as the inaccuracies of sampling, about 15 g. of the conditioned fabric is weighed out accurately and placed in a 1-liter r.b. flask fitted with a reflux condenser. About 200 g. (250 ml.) of the solvent is weighed into the flask, using a good solution balance. The mixture is then refluxed for 15 minutes to extract lime soap from the fabric. After cooling to a temperature convenient for handling, an aliquot of the solution is weighed into the titrating flask. About 90 g. (100 ml.) is a suitable aliquot and requires 8 to 10 drops of indicator. The results obtained by the two procedures check very well. The blank value obtained in the second procedure is smaller, indicating that the basic ash in the fabric is not extracted by the solvent. The results of either titration are expressed as milliequivalents of $HClO_4$ necessary to titrate the basic extract (lime soap) present in one gram of fabric. This value is multiplied by 10^4 for convenience in handling. Assuming lime soap to have the formula of neutral calcium oleate, a titration value of 100 corresponds to 0.3% lime soap on the fabric. The accuracy and reliability of the method have been checked in the absence of fabric by using purified Mg and Ca palmitates and in the presence of fabric by the usual ashing procedure.

Lime Soap Peptizing Power. The following simplified procedure for measuring the protective action of surfactants has been found to give results of excellent reproducibility. Solutions containing 1.0% low titer soap and 1.0% of the surfactant, respectively, are made up in distilled water. These are used to prepare a series of mixtures in which the ratio of soap to surfactant is progressively increased. Five ml. of each mixture is placed in a Nessler tube, and 45 ml. of 400 ppm. hard water is added. The tubes are inverted once, to mix the contents, and are allowed to stand for 30 minutes. At the end of this period they are inverted three times sharply, to provide agitation, and are then examined for visible clots of lime soap. The lowest percentage of surfactant which will prevent clotting of the lime soap is taken as the lime soap dispersing value of the surfactant. The influence of changes in temperature, agitation, or type of soap used is remarkably small. Care must be taken to avoid conditions where the surfactant itself is not completely soluble in the hard water. Alkyl arylsulfonates at low temperatures and nonionics at high temperatures are particularly troublesome in this respect. The above procedure is referred to in the following discussion as the Nessler tube test.

Materials. The three surface active materials used in this study were soap, an alkyl benzene sulfonate and an oleyl methyl tauride. The soap was a commercial brand of low-titer flake and was used without further purification. The alkyl benzene sulfonate was a commercial low-salt content product, analyzing 89% active ingredient, and was also used without further purification. The oleyl methyl tauride contained approximately 95% active ingredient and was prepared from the commercial material by extracting with ethanol.

Results and Discussion. In the Nessler tube tests the oleyl methyl tauride gave consistently excellent lime soap dispersing values, averaging about 8%. The alkyl benzene sulfonate gave values in the range of 70-80%, the poor duplicability accompanying the low absolute peptizing power. Soap itself proved to be an excellent peptizing agent for lime soap. In a modification of the Nessler tube test, solutions were made up to contain varying percentages of soap in 360 ppm. hard water (the hardness of the final solution in the standard test). When the added soap amounted to less than 0.2%, it all was precipitated and clotted. At 0.3% soap, as well as at higher concentrations, stable sols were produced. Between 0.2% and 0.3% the results were erratic and poorly reproducible. It requires in theory 0.22% soap to precipitate all the hardness from 360 ppm. hard water in the form of neutral lime soap. When 0.3% soap is added to 360 ppm. water, the final system presumably contains about 0.22% lime soap, 0.08% sodium soap, and no dissolved hardness. Under these conditions the lime soap is completely peptized.

In the first group of experiments dealing with deposition on fabric, hard water was used in both the washing step and the rinsing steps of the standard cycle. Figure 1 shows how the lime soap deposit builds up as the number of cycles is increased. In this series the bath contained 0.5% soap and no protective agent. It is apparent that as the number of cycles increases the rate of deposition progressively decreases, and after about 15 cycles it becomes quite small. This indicates a distinct limit to the amount of lime soap the fabric can hold under these operating conditions. For optimum convenience 10 cycles were chosen as the basis for further runs in this group.

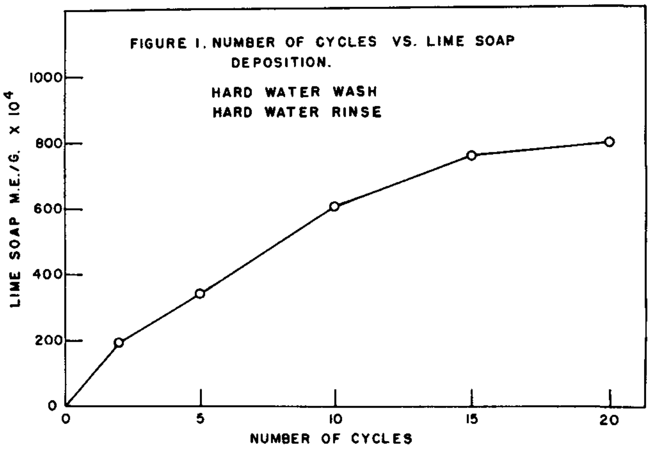
FIGURE 1. NUMBER OF CYCLES VS. LIME SOAP DEPOSITION.

The lime soap deposition was next determined as a function of the percentage of soap added to the bath. The results are shown in the upper curve of Figure 2. At concentrations lower than 0.15% the soap is completely flocculated in the washing bath and relatively little remains on the fabric after rinsing. In the range of 0.2-0.3% the conversion to lime soap should be nearly complete in the washing bath, and there should be relatively little further conversion in the rinses. At 0.4% and 0.5% the lime soap is completely peptized in the washing bath, and an excess of sodium soap is carried over to the rinses where precipitation is completed. Nevertheless the curve reaches a fairly good plateau at 0.2% soap. It is accordingly not clear from these data whether deposition of clotted soap in the washing step or precipitation "in situ" during the rinsing step is more important.

In another series of this first group, the results of which are also shown in Figure 2, the test surfactants

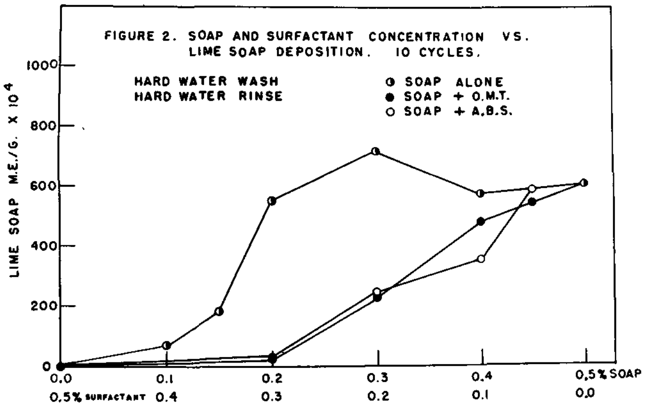
FIGURE 2. SOAP AND SURFACTANT CONCENTRATION VS. LIME SOAP DEPOSITION. 10 CYCLES.

were mixed with soap in varying proportions; the total concentrations of soap-plus-surfactant were held at 0.5%. It is noteworthy that the curves for oleyl methyl tauride (OMT) and alkyl benzene sulfonate (ABS) parallel each other quite closely in spite of the fact that the former product is a much better peptizing agent than the latter. At soap concentrations of 0.2% the OMT bath is clear and the ABS bath contains flocs of lime soap, but in neither case is an appreciable quantity of lime soap permanently deposited. At 0.4-0.45% soap, where both baths are clear, neither surfactant prevents the ultimate deposition which presumably takes place in the rinsing operations. A final series in this group involved washing with soap-surfactant mixtures in which the soap concentration was held constant at 0.3% and the surfactant concentration was varied from zero to 0.3%. The results are shown in Figure 3. The OMT and ABS curves are again almost superimposed. The soap concentration in this system is sufficiently high to remove all the hardness from the washing bath, and a considerable proportion of the deposition must take place in the rinsing step. Under these conditions it appears that lime soap deposition remains at a fairly high level even when the proportions of surfactant are large.

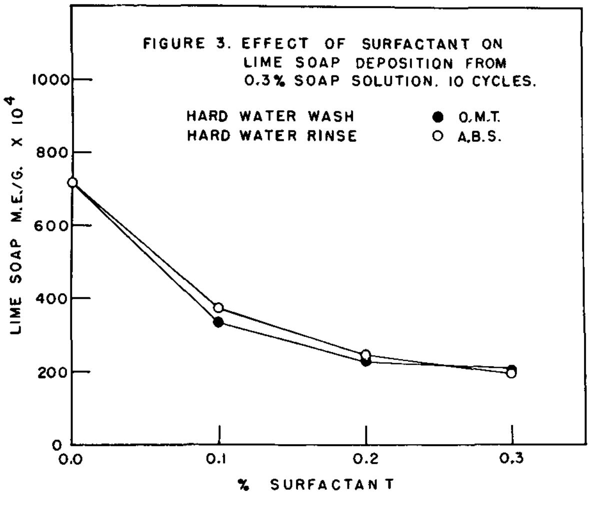
FIGURE 3. EFFECT OF SURFACTANT ON LIME SOAP DEPOSITION FROM 0.3% SOAP SOLUTION. 10 CYCLES.

The second group of tests, consisting of only one series, differed from the first group in that distilled water was used in the rinsing steps, and hard water was used only in the washing step. In this series soap alone was tested, and the lime soap depostion was plotted as a function of soap concentration. The results are shown in Figure 4. The portion of this curve ranging from zero to 0.2% soap concentration resembles the analogous portion of the soap curve in Figure 2. In this region all the sodium soap is being converted to lime soap in the washing step so that no dissolved soap remains in the washing liquor. The lime soap is being firmly deposited and is not removed by the distilled water rinses. At higher concentrations there is an excess of sodium soap present in the washing bath and the lime soap is peptized. During the distilled water rinse all the peptized lime soap which has not been absorbed is washed out. At 0.3% there is presumably insufficient excess sodium soap in the wash bath to prevent completely the adsorption of some lime soap.

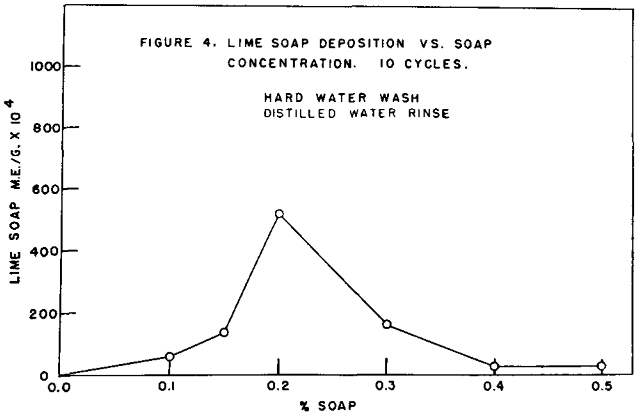
FIGURE 4. LIME SOAP DEPOSITION VS. SOAP CONCENTRATION. 10 CYCLES.

In the final group of experiments the washing was carried out in distilled water and the rinsing in hard water. This is a realistic set of conditions since it is feasible and common practice to include water softeners in washing compositions. The behavior of soap alone under these conditions is shown in Figure 5. Comparing this curve with the soap curve in Figure 2, it is apparent that precipitation "in situ" during rinsing leads to a firmly held deposit of lime soap whereas lime soap transferred to the fabric from a suspension is less firmly and/or less extensively retained.

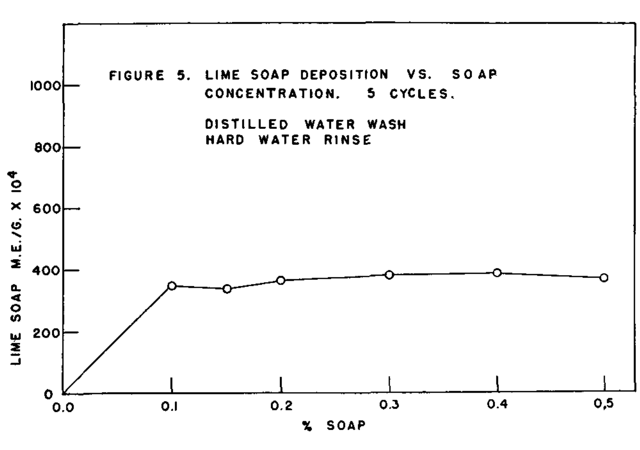
FIGURE 5. LIME SOAP DEPOSITION VS. SOAP CONCENTRATION. 5 CYCLES.

The effect of adding increasing amounts of surfactant to a 0.3% soap solution in this system is shown in Figure 6. Again there is no appreciable difference

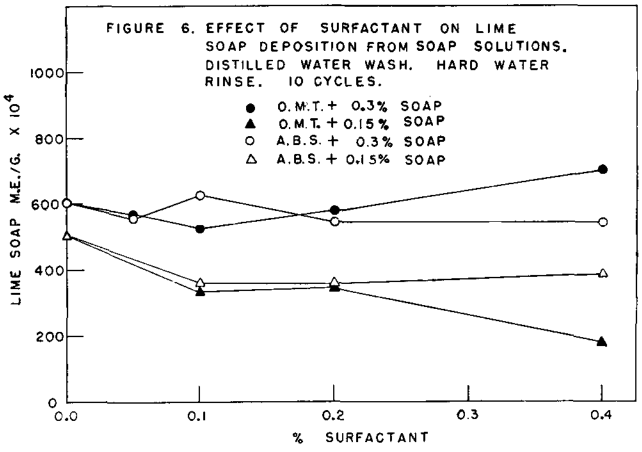

FIGURE 6. EFFECT OF SURFACTANT ON LIME SOAP DEPOSITION FROM SOAP SOLUTIONS. DISTILLED WATER WASH. HARD WATER RINSE. 10 CYCLES.

between OMT and ABS, and even when the ratio of surfactant to soap is 1.33, there is no appreciable decrease in the lime soap deposition.

When the concentration of soap is lowered to 0.15% the surfactants have a positive but relatively small effect in preventing lime soap deposition. Under these conditions OMT shows some advantage over ABS, but the advantage only becomes apparent at very high ratios of surfactant to soap.

Conclusions

These results appear to justify the following statements with regard to lime soap deposition and the influence of added surfactants.

1. Peptizing power, as exemplified by the Nessler tube test, is not a realistic index of the extent to which a surfactant will prevent firm deposition. A total concentrations of soap-plus-surfactant were held deposition resulting from a filtration effect, and this is of importance in many practical situations.

2. Clotted lime soap, in the absence of excess sodium soap or other protective agent, becomes firmly attached to the fabric. Clotted lime soap which has not been formed "in situ" does not become attached to the fabric in the presence of the non-peptizing surfactant ABS.

3. Lime soap which is peptized by the presence of excess sodium soap or peptizing surfactant does not become attached to the fabric.

4. It is very difficult to prevent the firm attachment of lime soap which is formed from sodium soap in the presence of the fabric, as during hard water rinsing. The presence of OMT or ABS in the sodium soap solution will diminish this deposition but only when the ratio of surfactant to soap is relatively high. There appears to be little practical difference between OMT and ABS in this respect, except when unusually high ratios of surfactant-to-soap are used.

Summary

A method is described for the direct volumetric estimation of lime soap on fabrics. Experimental evidence is presented to demonstrate the conditions under which lime soap may become firmly attached to the fabric. The effects of two anionic surfactant additives, oleyl methyl tauride and alkyl benzene sulfonate, in preventing firm lime soap deposition have been described.

Acknowledgment

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The Composition of Fat From Icterus Swine[1,2]

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IT is not uncommon for a hog carcass to be condemned in the packing plant on post-mortem inspection. Sometimes the condemnation is based on soft and yellow-colored fat. Beadle, Wilder, and Kraybill (1) reported on the fatty acid composition of certain swine condemned because of soft yellow fat but exhibiting no manifestations of disease. They found that these fats contained approximately 10 times the amount of linolenic acid found in normal hog fat. This high proportion of polyunsaturated fatty acid was ascribed to dietary factors since it is well-known that the pig can incorporate fatty acids from its diet into its depot fats. They observed that rats fed a diet containing flaxseed deposited a heavy concentration of trienoic acids in the fat. Recently Lalor, Leoschke, and Elvehjem (5) observed that young mink, when fed a diet rich in trienoic fatty acids, developed soft yellow fat with a high trienoic fatty acid content. Shorland (7) has suggested the term "homolipoid" for fats which readily incorporate the fatty acids present in the dietary fat. While the condemnation of animals which have soft yellow fat due to dietary factors is relatively rare, there are numerous swine condemned as unfit for human use because of conditions of disease. Many of these animals are known as "icterus swine" because of the jaundiced or yellowish skin, fat, and liver. The cause of the jaundice may be infectious in nature, or it may be obstructive resulting from an obstruction of the common bile duct. Obstruction of the bile duct may in many cases be due to worm infestations. It was thought to be of interest to determine whether the yellow fat in "icterus swine" had an abnormal fatty acid composition.

Experimental

Fats from 18 animals classed as "icterus swine" were examined. The iodine values and fatty acid com-

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[1] Journal Paper No. 47, American Meat Institute Foundation.

[2] Presented at 25th Fall Meeting of the American Oil Chemists' Society, Chicago, Ill., Oct. 8-11, 1951.