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Use of Soap in Modern Detergent Formulations

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Detergent formulations of soap as major ingredient in combination with a lime soap dispersing agent and detergent builders found to be equivalent in detergency to commercial household laundry detergents containing phosphate builders.

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TALLOW SOAP has been used as the principal laundry detergent from the dawn of civilization until the end of World War II, at which time phosphate built synthetic detergents became commercially available. One of the reasons for the rapid acceptance of phosphate built synthetic detergents was their improved performance over a range of water hardness and temperature compared with soap.

If the formation of lime soap curd during washing and rinsing could be prevented and the detergency of soap in cooler water improved, soap based detergents would become competitive with phosphate built synthetic detergents in both cleaning performance and cost. In response to the needs of the times for a phosphate-free detergent based upon replenishable agricultural by-products the Eastern Marketing and Nutrition Research Division of the U.S. Department of Agriculture initiated research to achieve the above goals for a soap based detergent formulation.

* Based on paper presented during 58th mid-year meeting, Chemical Specialties Manufacturers Association, Chicago, May 17.

Lime Soap Dispersants

The basic concept utilized in these studies is the addition of a lime soap dispersing agent (lsda) to laundry soap formulations. This approach was suggested by Linfield in 1959 (1) for the addition of nonionic or anionic surfactants to laundry soap; a more recent publication by Mayhew and Burnette (2) describes the incorporation of acyl isethionates into soap bars and acyl N-methyltaurides into various types of detergents. A simple explanation of the action of an lsda in a soap micelle was given by Stirton and coworkers (3).

In general, an lsda possesses a structure in which a long hydrophobic chain terminates in a bulky hydrophilic group or in two adjacent anionic groups as shown in Figure I which shows in a simplified way how lsda's might act. In the absence of a lime soap dispersing agent the typical soap micelle (B) formed from the oriented molecules (A), is changed by hard water to an inverted phase (C) which leads to separation of lime soap curds. In the presence of the lime soap dispersing agent inversion is prevented, possibly through formation of a mixed micelle (D) in which the proper curvature is maintained by the bulky hydrophiles of the lime soap dispersing agent.

The first systematic study of detergent systems based upon soap-lsda-builder combinations was carried out by Bistline (4) and coworkers of this laboratory. The addition of an lsda such

Figure 1

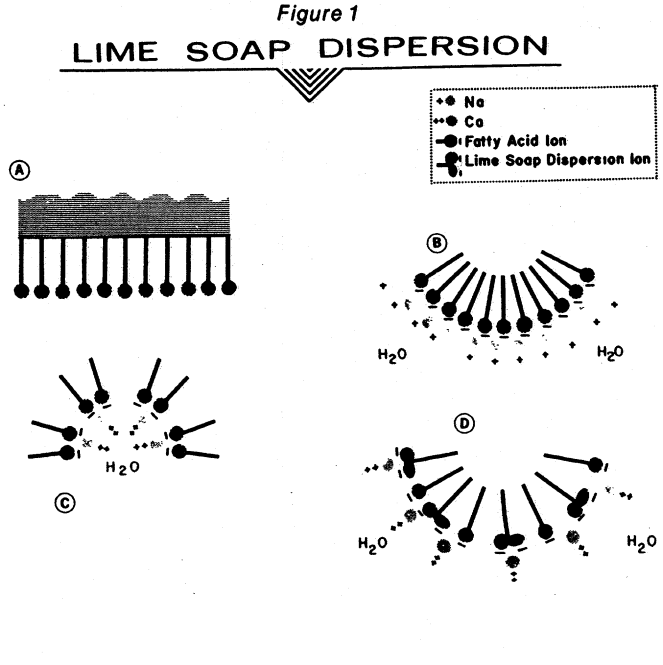


Figure 2. Detergency of ternary system of soap/TMS/sodium metasilicate on Testfabrics' soiled cotton fabric.

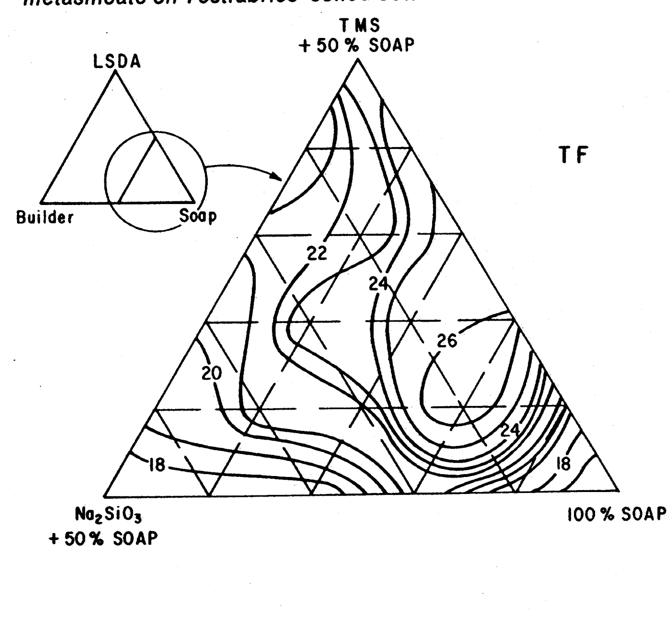


Table I. Lime Soap Dispersing Ability of Various Lime Soap Dispersing Agents

Lime Soap Dispersing Agent	Borghetty-Bergman Value
TMS	9
TAM	5
IgT	5
LAS	40

Table I are the number of grams of lsda which have to be added to 100g of sodium oleate just to prevent the formation of a lime soap curd in hard water. Therefore, a low Borghetty-Bergman value corresponds to high lime soap dispersing ability. TMS, TAM and IgT are all effective lsda's in contrast to a commercial linear alkylbenzenesulfonate (LAS) which is much less efficient and hence not suitable for the soap based detergent formulations.

Detergent Formulation Studies

The formulation studies were accompanied by detergency evaluations in order to select the most suitable formulations. The detergency screening methodology was as follows: five swatches of each of three standard soiled cloths, U.S. Testing cotton, EMPA 101 cotton and Testfabrics cotton-polyester with permapress finish were placed in each Tergotometer beaker. For screening purposes all evaluations were conducted at 120° F., 300 ppm water hardness and at total detergent concentration of 0.2%. This set of experimental conditions was chosen because previous experience had shown that it is difficult to obtain good detergency with soap formulations under these conditions.

Table III. Builder Effects of Various Sodium Silicates upon a 75/25 Soap/IgT Blend

% Builder Added	TF	ΔR EMPA	UST
0%	14.2	22.2	6.0
+ 10% 1:1.3 sod. silicate	16.9	33.8	8.5
+ 15% 1:1.3 sod. silicate	15.1	38.4	9.0
+ 20% 1:1.3 sod. silicate	14.9	38.2	6.1
+ 10% 1:1.6 sod. silicate	17.0	35.0	8.9
+ 15% 1:1.6 sod. silicate	15.4	37.3	8.1
+ 20% 1:1.6 sod. silicate	15.0	38.9	8.1
+ 10% 1:2.4 sod. silicate	19.0	32.3	8.7
+ 15% 1:2.4 sod. silicate	18.5	34.4	7.8
+ 20% 1:2.4 sod. silicate	16.5	36.4	7.7

A more detailed formulation study was carried out with TMS as the lsda. Initially binary mixtures of soap and TMS were evaluated for detergency. Subsequently various builders were added in fixed increments to each binary mixture. The results of this study are shown in Table II.

Builders chosen for this study are quite conventional. Sodium tripolyphosphate (STPP) was included for comparison; also STPP built soap formulations would contain far less phosphate than the commercial phosphate built products. Trisodium nitrilotriacetate (NTA) was included in this study, since its future is still undecided from a human safety viewpoint. Sodium citrate has been suggested as a detergent builder and is considered to be a safe detergent additive. Sodium silicates have been components of detergents for many years and a comparison between metasilicate and a less alkaline silicate ($1Na_2O$:1.6 SiO_2) proved to be particularly interesting.

As Table II shows a blend of 75-80 parts of soap with 25-20 parts of TMS is required for good detergency even if no builder is used. As far as builder effectiveness is concerned, sodium citrate does not appear to be a very useful builder for soap based systems. Sodium tripolyphosphate is slightly more effective than citrate. NTA added to an 80/20 soap/TMS blend is unusually effective in washing cotton-polyester permanent press fabric, but a 15% addition of NTA to the same soap-TMS blend is required for good EMPA cotton detergency.

The two silicate builders appear to be most effective in soap based systems. A 10% addition of metasilicate to a 75/25 soap/TMS blend achieves a cotton polyester detergency very close to that of the NTA mentioned above as well as that of a commercial phosphate built detergent designated here as Control A. The 1:1.6 ratio sodium silicate gave the best EMPA 101 cotton detergency at a 15% addition level to the 75/25

Table II

Detergency (Δ R Values) of Ternary Soap-TMS-Builder Formulations

Builder Added	Soap/TMS Ratio 75/25 TF	EMPA	UST	Soap/TMS Ratio 80/20 TF	EMPA	UST	Soap/TMS Ratio 85/15 TF	EMPA	UST	Soap/TMS Ratio 90/10 TF	EMPA	UST
+ 0%	16.9	16.6	7.7	16.1	21.3	7.5	10.1	18.4	4.8	8.3	19.5	2.7
+ 5% STPP	15.7	18.0	6.4	15.2	22.1	5.4	9.6	22.5	5.1	4.3	11.6	2.1
+ 10% STPP	15.4	18.7	6.6	13.3	23.2	4.3	9.1	19.7	3.2	3.6	12.2	1.3
+ 15% STPP	12.8	19.2	5.6	11.1	27.8	4.7	9.1	22.3	3.3	2.6	12.3	0.3
+ 5% Sodium Metasilicate	18.9	15.4	6.6	17.0	19.3	7.1	13.0	19.5	5.9	6.3	10.7	3.4
+ 10% Sodium Metasilicate	19.3	19.8	7.0	16.2	20.5	5.6	11.2	21.3	5.6	5.1	12.0	3.6
+ 15% Sodium Metasilicate	17.9	20.7	6.5	14.0	17.9	5.1	8.1	17.9	5.0	2.4	11.0	1.5
+ 5% (1:1.6) Sod. Silicate	16.9	21.6	7.9	13.8	18.5	6.0	10.0	23.7	6.5	9.3	21.0	5.2
+ 10% (1:1.6) Sod. Silicate	14.4	32.9	5.3	13.2	30.0	5.2	10.2	23.2	3.9	10.0	23.0	5.6
+ 15% (1:1.6) Sod. Silicate	14.1	34.2	6.4	10.5	22.2	4.8	10.2	22.8	3.1	10.5	32.1	5.5
+ 5% NTA	20.4	17.3	8.3	21.5	22.7	5.4	17.6	22.1	6.4	8.5	16.1	2.0
+ 10% NTA	21.5	20.5	7.1	18.6	22.5	6.3	14.9	26.1	5.4	7.5	18.3	4.4
+ 15% NTA	19.6	16.8	6.4	14.8	33.7	5.6	13.8	22.8	5.1	4.5	14.8	2.4
+ 5% Sod. Citrate	15.7	19.0	7.8	14.3	17.8	7.3	9.2	20.4	6.1	6.5	20.4	4.4
+ 10% Sod. Citrate	17.5	18.0	5.0	13.3	19.4	5.4	9.2	16.1	4.3	7.3	14.1	3.4
+ 15% Sod. Citrate	14.5	18.8	5.5	11.1	21.3	4.6	9.4	20.1	4.3	6.7	18.8	2.9
Control A	20.3	36.3	6.3									

Table IV. Soap Based Detergent Composition (dry basis)

Tallow soap	64%
Lsda	19%
1:1.6 Sodium silicate	14%
CMC	1%
Brighteners, misc. impurities	2%

soap/TMS blend. This type of formulation also gave adequate U.S. Testing cotton detergency equal to that of the control. Only the Testfabrics cotton-polyester detergency was somewhat inferior to that of the control. Since the 1:1.6 silicate is less alkaline than the metasilicate its use seemed preferable from a safety standpoint.

When IgT was employed as the lime soap dispersing agent the detergency results were very similar to those obtained with TMS. The 75/25 soap/IgT ratio gave the highest detergency values. A comparison of the builder effects of various types of sodium silicate is shown in Table III.

It would appear from the data in Table III that the 1:2.4 ratio silicate gave the best Testfabrics detergency whereas the 1:1.3 silicate gave the highest EMPA cotton detergency. Since the 1:1.3 sodium silicate is not a commercially available material, we settled on the 1:1.6 ratio as a good compromise. Fortuitously this turned out to be a good choice, since it was found that the detergency behavior of drum-dried formulations deviates slightly from the observations reported in Tables II and III. These were obtained by adding each ingredient separately to the Tergotometer beakers. The drying of detergent slurries had an adverse effect on the detergency of those formulations containing the 1:2.4 sodium silicate. We have not investigated the cause of this phenomenon as yet except to establish that the decreased detergency is due to an interaction between the 1:2.4 silicate and tallow soap.

The third lime soap dispersing agent (TAM) behaved very much like TMS and IgT, so that a report on its detergency behavior does not need to be repeated here. On the basis of the foregoing, the formulation shown in Table IV was chosen for scaling up in pilot plant drum-drying and spray-drying equipment.

Soap Based Detergents Properties

The chemical properties and performance characteristics of the three spray-dried detergents were examined and compared with those of commercial household detergents (Controls A,

Table V. Comparative Alkalinities of Detergent Formulations

Detergent	% NaOH Total Alkalinity	% NaOH Reserve Alkalinity	pH of 0.1% Solution
TAM Formulation	15.71	6.49	10.2
TMS Formulation	15.83	6.32	10.4
IgT Formulation	16.14	6.65	10.5
Control A	13.58	4.55	10.2
Control B	10.39	3.49	10.1
Control C	54.09	27.49	11.0

Figure 4. Detergency behavior of soap based detergent and controls over a concentration range and at three water hardnesses on EMPA 101 soiled cotton fabric.

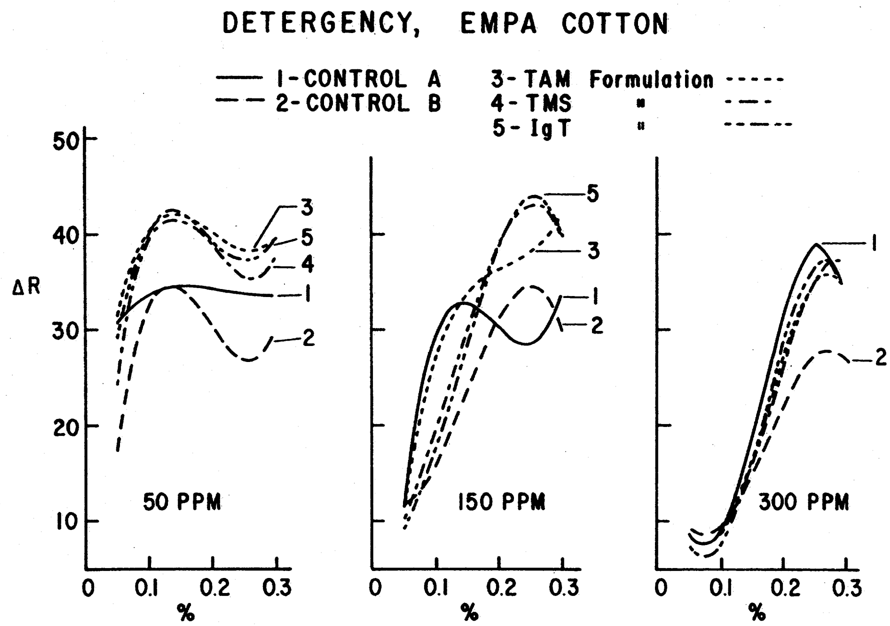
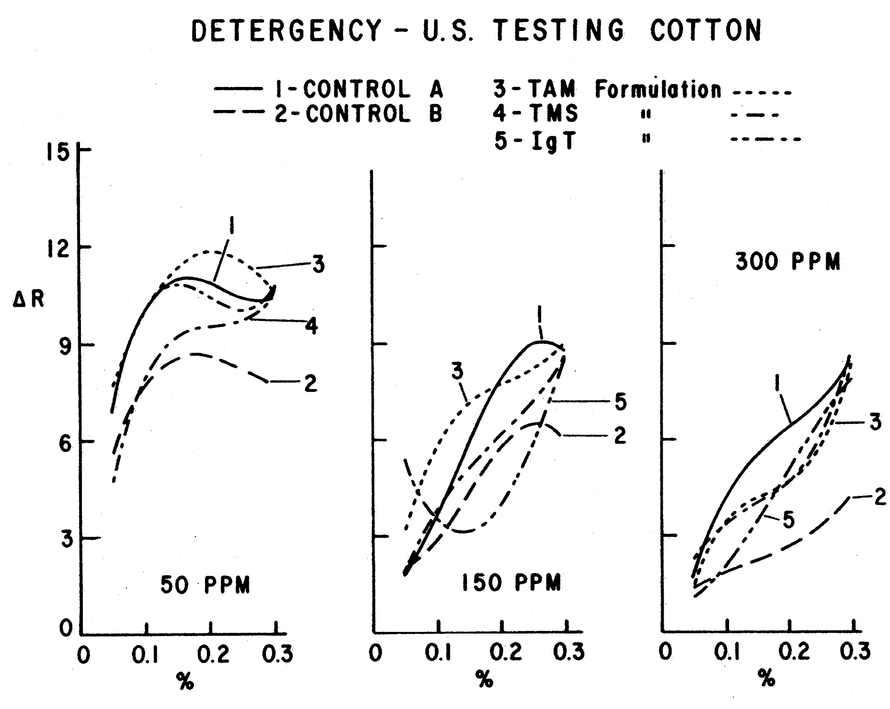


Figure 5. Detergency behavior of soap based detergents and controls over a concentration range and at three water hardnesses on U.S. Testing soiled cotton cloth.



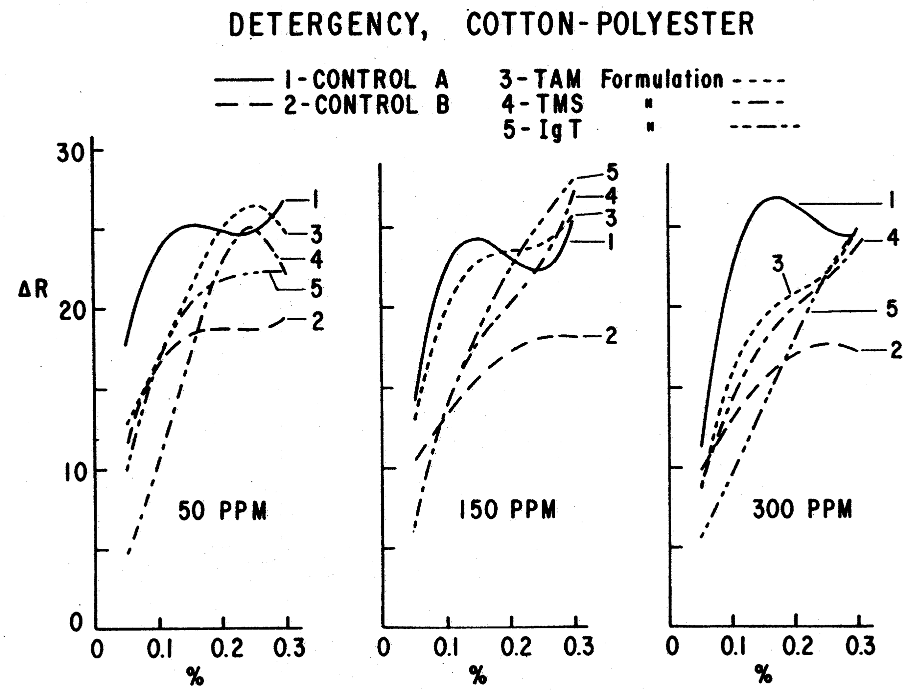


Figure 6. Detergency behavior of soap based detergents and controls over a concentrated range at three water hardnesses on Testfabrics' soiled cotton-polyester permanent press finish cloth.

B and C). A was the phosphate-built anionic detergent which had been used throughout this study, whereas Control B was a phosphate-built nonionic detergent. Control C was a sodium carbonate built nonionic detergent formulation. A comparison of the alkalinity of the detergents is given in Table V. Total alkalinity refers to values obtained by titrating to a pH of 4, whereas reserve alkalinity refers to values obtained by titration to pH 9.5 As is obvious from Table V, the soap based formulations are not appreciably more alkaline than Controls A and B and substantially less alkaline than C. Alkalinity in terms of pH of use dilutions likewise is in line with Controls A and B and lower than C. Thus, in summary, the soap base detergents can be expected to be as safe as conventional phosphate-built detergents from an alkalinity standpoint.

The detergency behavior of the three spray dried detergents was compared with that of Controls A and B using the three test cloths as described above. However, detergency values were obtained at four concentrations 0.05%, 0.1%, 0.2% and 0.3% and at three water hardnesses 50 ppm, 150 ppm and 300 ppm. The results are shown graphically in Figures 4, 5 and 6.

The three soap-based detergents are about on a par with Control A, except in the case of the Testfabrics cotton-polyester blend at 300 ppm, where A is slightly superior. Control B is inferior to all three soap-based formulations. While single wash tests with standard soiled cloths in a Tergotometer do not yield absolute values with respect to the cleaning ability of detergents, the evidence nevertheless indicates that the soap-based detergents are likely to be as effective as conventional phosphate built household detergents. As an additional check on the detergency, a series of multiwash tests was carried out according to the method of Schwartz and Berch (9). In this test, cotton and cotton-polyester blend with permanent press finish were soiled with vacuum cleaner dirt and then washed in 0.2% detergent solutions at 300 ppm water hardness. Soil redeposition was determined by washing clean swatches of both types of fabric along with the soiled ones in the Tergotometer. The soiling and washing cycles were then repeated five more times. The swatches designated for the soil redeposition measurements were, of course, not soiled but merely washed together with the soiled swatches. The reflectance difference between the original white fabric and the successively soiled and washed fabric is an indication of the grayness development on the fabric. In the case of the swatches which were washed together with the other swatches but not soiled, there is a grayness buildup due to redeposition of soil from the wash solution. The results appear in Table VI, which shows that there is no substantial difference in washing performance between the two phosphate built detergents (Controls A and B) and the three soap based detergents. Thus, the multiwash detergency data verify the results obtained by washing standard soiled swatches in single washes.

Since soap washes poorly at temperatures lower than 120° F., it was important to determine whether the performance of soap/lsda/builder formulations is also temperature sensitive. The data given in Table VII show that at 60 and 90° F. and at 300 ppm water hardness two of the soap based formulations perform as well on the two cotton soils as does Control A. In the case of the Testfabrics cotton-polyester fabric the control is somewhat superior to the

Table VI. Grayness Buildup in 6 Successive Washes Due to Soiling and Soil Redeposition

	— ΔR			
	Cotton		Cotton-Polyester Blend with Permanent-Press Finish	
	Soiling	Redeposition	Soiling	Redeposition
Control A	14.8	7.3	9.3	6.0
Control B	13.2	5.4	11.4	5.8
TAM Form	14.3	7.8	10.1	6.1
IgT Form	13.9	7.2	10.0	6.3
TMS Form	14.9	7.7	11.3	6.8

Table VII. Low Temperature Detergency at 300 ppm Water Hardness, ° F

	Detergency (ΔR)					
	EMPA		U.S.T.		TF	
Formulation	60°	90°	60°	90°	60°	90°
TMS Formulation	12.6	25.6	6.4	8.0	18.6	18.1
TAM Formulation	12.8	26.2	5.4	8.0	17.9	18.9
CONTROL A	13.4	24.6	7.3	8.7	25.0	23.3

two test detergents. Washing at low temperatures is therefore analogous to washing at 120° F. The IgT formulation was not tested for detergency at low temperature.

Washing with soap alone, particularly in hard water, shows up another weakness of soap, namely the precipitation of lime soap in the fabric and upon the surface of the washing machine during the rinse cycle. This precipitation usually causes a buildup of grayness due to redeposition of soil. The multiwash data of Table VI show no excessive grayness buildup for the soap based detergents. Another check on absence of precipitation was obtained through turbidity measurements as shown in Figure 7. Blends of 75% sodium oleate and 25% of each of the three lsda's were dissolved in 300 ppm hard water to a concentration of 0.2% and the turbidity measured. Subsequently the solutions were diluted further to 0.02% and 0.002%. Figure 7 shows that the turbidity dropped with successive dilutions. Turbidity values remained unchanged for at least one hour over the concentration range studied; no visible precipitate was observed.

Biodegradability Studies

The biodegradability of the three soap-based detergent formulations, the three lsda's of this study and an LAS control was determined by the oxygen depletion procedure of Dias and Alexander (10) in which the rate and the amount of oxygen depletion indicates the ease of biodegradability. This method was used, because the more conventional presumptive test of the Soap and Detergent Association (11) is not applicable to soap.

In this study the concentration of each test material solution was adjusted so as to give a total carbon content of 2 mg/l. This requires an oxygen consumption of 5.3 mg/l if certain interferences could be ruled out. Unfortunately the situation is complicated by oxygen uptake by the microorganism cells and by nitrification. Although a blank corresponding to the oxygen consumption by the sludge organisms had been subtracted from the observed data it must be borne in mind that biological data are not very precise. In studying the data of Table VIII changes in the rates of oxygen consumption rather than the absolute consumption values should be looked for. Thus, it will be observed that all materials except LAS showed a substantial oxygen uptake after two days corresponding to a biodegradation of at least 50%, whereas nine days were required before LAS attained a similar level of biodegradation. After the fifth day the rate of biodegradation generally slowed down and the significance of the observations thereafter is somewhat doubtful.

Table IX. Biodegradability of Lime Soap Dispersing Agents by the S.D.A. Method (11)

Lime Soap Dispersing Agent	% Degradation after 7 days
TMS	100
TAM	100
IgT	100
LAS (control)	92

Since the biodegradability of LAS is considered adequate from a water pollution standpoint it can be concluded that the test lsda's as well as the formulated soap-based detergents are acceptable and, in fact, preferable as far as water pollution potential is concerned.

The biodegradability of the individual lsda's was also determined with the aid of the presumptive test of the Soap and Detergent Association (1) as shown in Table IX. The test results do not tell the entire story. Actually the test materials were completely degraded during the two day acclimatization period.

Summary

It has been shown that tallow soap based detergents can be formulated with the aid of lime soap dispersing agents and silicate builders to give detergent performance which is equal to that of commercial household detergents built with phosphate. The soap-based detergents possess none of the objectionable properties of soap alone. Their ready biodegradability and absence of phosphates and other potentially objectionable components should make them highly acceptable from a water pollution point of view.

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Figure 7. Turbidity of 75% sodium oleate/25% lsda blend solutions upon successive dilution with 300 ppm hard water.

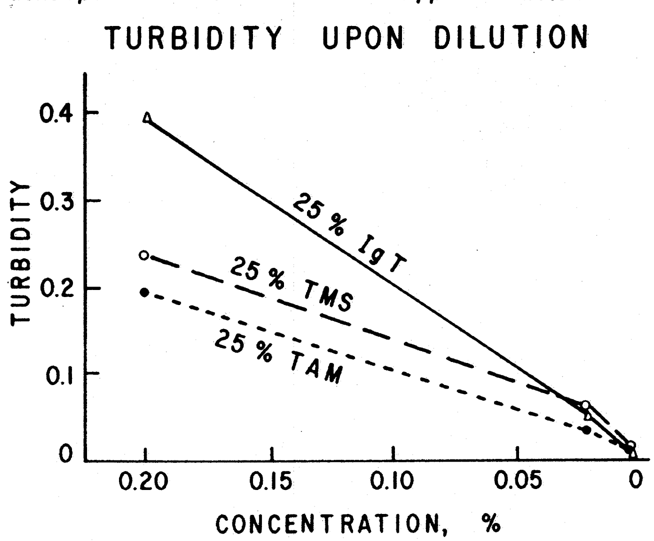

Table VIII. Biodegradability by Oxygen Depletion

Test Sample	Total Amount of Oxygen in mg/1 Consumed on Day			
	2	5	9	15
Tallow Soap	3.8	4.1	4.8	5.7
LAS	0.1	1.6	3.1	3.9
TMS Formulation	2.9	3.5	3.9	4.3
TAM Formulation	2.7	3.2	3.6	3.9
IgT Formulation	2.7	3.1	3.7	4.2
TMS Active Ingredient	2.8	4.2	5.0	
TAM Active Ingredient	3.5	4.9	6.5	
IgT Active Ingredient	3.6	5.6	6.5	