experimental results are shown in Table 1. Four reagents prepared from products 3, 5, 11, and 14 and the three reagents prepared from the recrystallized products gave comparable results. The averages of these values were employed as the basis of comparison with the remaining reagents under investigation. In the last column of Table 1 it will be observed that product 2 gave thiocyanogen values that were approximately one unit low, while the values obtained with products 6, 15, and 16 averaged 3.2 units lower than the mean values.

Summary

A new and improved method for the preparation of a pure and stable lead thiocyanate in practically theoretical yield has been described.

A comprehensive investigation of other published methods has been reported and preparations of lead thiocyanate made by these methods have been compared with the improved compound and various commercial products.

All of the products were assayed for purity on the basis of their chemical analyses and tests were made of their capacity for saturating double bonds in cottonseed, peanut, and soybean oils.

The lead thiocyanate prepared according to the recommended procedure was found superior to all the other products in stability, purity, and ability to produce dependable and reproducible thiocyanogen values.

It has been demonstrated that the ratio of lead ions to thiocyanogen ions and the order of addition of these ions to each other are of major importance in the preparation of pure lead thiocyanate.

Acknowledgment

The authors express their appreciation to M. E. Jefferson and Florence B. Kreeger for the microscopic examinations and preparation of the photomicrographs, to R. T. O'Connor and Dorothy Heinzelman for the spectroscopic data, and to R. Robinson and L. Brown for the sulfur determinations.

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Builders With Synthetic Detergents*

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ADJUNCTS to soap have their own voluminous literature so that no attempt will be made to review this work except as it pertains to the present discussion. In the generally accepted sense of the word, "builders" are considered as materials which, when added to soap, improve its utility. Differentiated from builders are "fillers" whose only virtues lie in their properties as extenders or diluents and result in no improvement in the surface activity of the soap to which they are added. The builders with which this paper will deal are comprised essentially of the class of water-soluble electrolyte compositions.

Relatively few papers have been published concerning combinations of builders with synthetic detergents although a working theory exists which explains the action of builders both for soap and these newer agents. The effects produced by builders upon surface active agents may readily be traced experimentally by measurement of lather, surface and interfacial tensions, wetting and detergency. There are many methods for measuring each of these several properties, and it is not the present purpose critically to review them but to show that builders produce improvement and to indicate the development of a theory to explain these effects. This theory will be reviewed, and experimental evidence will be described showing the extent to which certain builders affect the surface activity of an alkyl benzene sulfonate.

Literature Review

Earlier investigators worked with soaps and found that the addition of 0.2% sodium chloride (1) increased the lathering action of sodium oleate and decreased its surface tension although greater than 2% was required to provide a small increase in emulsifying action. Sodium carbonate in 2% quantities sharply increased lather and decreased surface tension. Other workers (2) found that the detersive action of a 0.25% soap solution at first was increased by the addition of sodium chloride, sodium sulfate or disodium phosphate, then was decreased upon further addition of these electrolytes. They found that effectiveness of the electrolyte was approximately proportional to the valence of the anion of the added salt. No attempt will be made to follow this trend further except to indicate that alkaline electrolytes in general tend to conform to these observations. Subsequent discussion is concerned with the effect of electrolyte builders upon synthetic detergents.

Study of the effect of electrolytes upon the surface activity of synthetic detergents has been made, and

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some interesting observations have been developed into several well established generalizations. In the determination (3) of the effect of electrolytes upon sulfonated alcohols it was found that the cleansing power of a given detergent at a certain concentration was first improved, then was lowered as the salt concentration was increased. In general it was concluded that increase in detergent power depended upon the valency of the added cations. Other investigators (4), also using alcohol sulfates, extended these findings with regard to the effect of the valency of added cations upon wetting times by the canvas disc method, surface tension lowering, foaming and detergency. Their results showed that continued addition of electrolyte, to a constant concentration of detergent, first increased detergency to a maximum, followed by a decrease as the added electrolyte passed a critical limit. Other workers (5) with sodium alkyl sulfonates found that sodium chloride decreased solubility, owing to the common-ion effect, and increased the temperature and decreased the concentration at which micelles begin to form. The micelles thus formed are stabilized by NaCl addition through a lowering of the electrical charge (6).

It was demonstrated (7) that addition of sodium, calcium and magnesium chlorides or sodium sulfate to the diamyl ester of the sodium salt of sulfosuccinic acid (Aerosol AY) resulted in a substantial improvement in surface and interfacial tension measurements.

It was found (8) that combination of electrolytes with Igepon T ($C_{17}H_{33}CONCH_3C_2H_4SO_3Na$) promoted micelle formation, acting analogously to the Schulze-Hardy rule for the coagulation of colloids by oppositely charged ions: thus the order of effectiveness is decreased progressively from trivalent to monovalent ions.

Other workers (9) have developed a mathematical treatment of these effects and showed that in the presence of electrolytes the potential energy of dissolved detergent ions is lowered by concentration about them of ions of the opposite sign (Debye-Huckel) but that the potential energy of detergent ions in the surface is lowered to a much greater extent. The amount of detergent in the surface in equilibrium with a given bulk concentration depends upon the difference in potential energy of a detergent ion in the two places. The greater lowering of the potential energy of the molecules in the surface results in displacement of the equilibrium in favor of the surface giving greater surface pressures and increased detergency. This corresponds to orientation of the detergent ion at the interface involved.

Addition of sodium chloride (4) will not yield greater detergency than can be obtained with higher concentrations of same detergent alone, but this work shows that bivalent cations are more effective detergent aids in their case than equivalent concentrations of monovalent compounds. Sodium chloride (5) will restore detergent power to a solution rendered inactive by a moderate excess of bivalent ion since the bivalent ion salts are more soluble in sodium chloride solution than in water.

An interesting proof by another technic (10) that the presence of an electrolyte resulted in increased solubilization of a dye (increased surface activity) when treated with solutions of nearly pure or sodium sulfate-containing alkyl aryl sulfonate follow:

Sample	Solubility of orange OT in 1% aqueous solution at 25°C. (mg. dye/100 c.c. solution)
Nacconol FSNO (nearly pure alkylaryl sulfonate)	3.8
Nacconol NR (contains sodium sulfate)	16.1

Although this paper is limited to electrolyte builders, it is of interest that non-electrolyte builders such as solvents improve detergency. The ability of soap solutions to dissolve generally water-insoluble organic solvents has been the subject of many investigations, and the method is widely used in industry. The same technic may be employed utilizing certain synthetic detergents (11) broadening the possible utility of this type of combination.

Theory

The theory covering the effect of addition of electrolyte follows in condensed form. The surface activity of soaps and ionic synthetic detergents is affected by the valency of added cation or anion. Improvement in surface activity resulting from added ions reaches a maximum, beyond which activity is decreased: the greater the valency of the ion, the less the amount of electrolyte required to reach this peak. This effect conforms to promotion of micelle formation according to the Schulze-Hardy rule for coagulation of colloids by oppositely charged ions. Surface activity is increased by the presence of electrolytes providing a lowering in potential energy of the dissolved detergent ions at the surface, which results in displacement of equilibrium in favor of the surface, giving greater surface pressures with resultant increased surface activity.

Already reported effects of builders upon surface tension, lather, wetting and detergency have been described for soap and for certain types of anionic synthetic detergents. That these effects are also attained when builders are added to the alkyl benzene sulfonate type of synthetic detergent will be apparent from the following data.

Experimental Work with Alkyl Benzene Sulfonate

The synthetic detergent described herein is comprised essentially of dodecyl benzene sodium sulfonate, the Santomerse No. 3 type being essentially 99+% pure, while Santomerse No. 1 contains a minimum of 40% active ingredient, the balance being essentially sodium sulfate.

TABLE I.
Lather Values.

	25 ± 0.2°C. Concentration 0.05% (Lather Height in Cms.)			
	50 p.p.m. water		300 p.p.m. water	
	At once	After 5 mins.	At once	After 5 mins.
Santomerse No. 3	13.2	12.8	13.5	12.8
Santomerse No. 1	15.7	15.1	9.8	9.4

Lather Values: The lather values shown in Table I were obtained through use of the apparatus described by Ross and Miles (12). It is very apparent for 50 p.p.m. water that a reduction to 40% active (for Santomerse No. 1) and the addition of sodium sulfate has not resulted in reduced lather but rather in a greater volume of foam. The poorer results in 300 p.p.m. hard water may be explained upon three bases: First, that the test is operated at the critical minimum concentration; second, that there is an excess of electrolyte at this extremely low concentration; and third, that insufficient active ingredient is present for Santomerse No. 1 at the water hardness used (below the critical amount necessary).

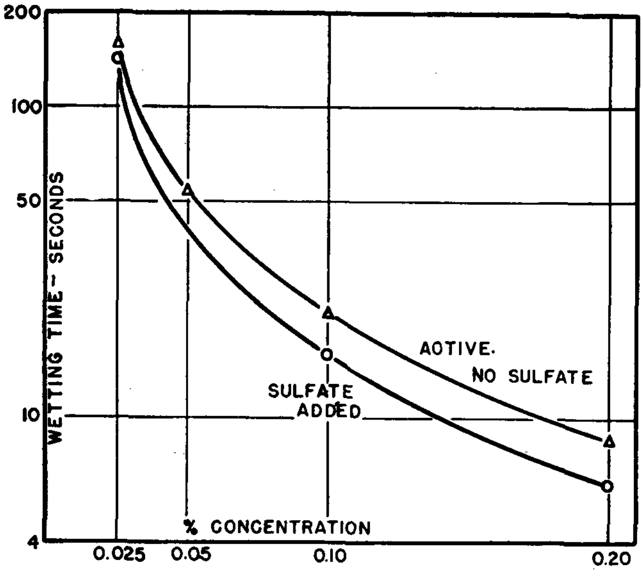

Fig. 1. Effect of sodium sulfate on wetting time. Canvas Disc Test.

These data then show that this type of compound conforms to theory as to lather but that other effects are produced when critically low concentrations are observed under hard water conditions (where the relatively more effective electrolyte Ca and Mg ions are present).

Surface and Interfacial Tension Measurements: According to theory the addition of electrolyte will result in a reduction of surface and interfacial tension values. Experiments were made with electrolytes and alkyl benzene sulfonate to verify this effect. The active ingredient was maintained constant throughout, diluting it either with water or with water and sufficient electrolyte to maintain solid concentrations at the percentages observed in Table II.

TABLE II.
Surface and Interfacial Tension Measurements.
(By duNouy Tensiometer)

Builder	Surface tension (Corrected according to Harkins and Jordan)			Interfacial tension (Nujol)		
	% concentration			% concentration		
	1.0	0.25	0.0625	1.0	0.25	0.0625
*None	32.0	31.2	30.3	5.2	3.5	3.1
NaCl	28.4	29.7	31.6	2.5	2.5	3.5
Na_2SO_4	29.2	30.2	30.4	2.9	2.8	3.3
Na_2CO_3	28.5	30.3	30.9	2.7	3.6	5.1
$Na_4P_2O_7$	29.4	30.6	34.8	2.7	4.3	8.4

* Active ingredient concentration throughout is 0.4 at 1.0%, 0.1 at 0.25% and 0.025 at 0.0625%.

It is interesting to note that these tests conform to theory in that there is actual reduction in surface or interfacial tension values so long as the critical concentration is not passed. However, when this concentration (usually 0.25%) is passed surface tensions are equal to, or higher than, those for the unbuilt product. The single exception to this generalization is that with tetrasodium pyrophosphate, but here again theory is met since smaller amounts of polyvalent anion will tend to result in optimum decrease in surface tension values as the critical point of addition is quickly passed.

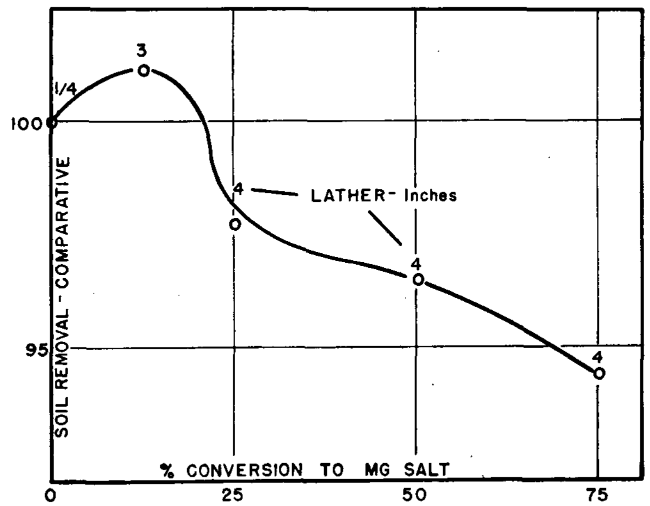

Fig. 2. Effect of magnesium chloride on detergency.

The effect of pH or alkalinity is apparent in interfacial tension values at 0.25% concentration since both the carbonate and pyrophosphate combinations are equal to, or greater than, the unbuilt product. The effect of valency of anion is apparent when a comparison is made between the chloride, sulfate (or carbonate), and pyrophosphate results.

Wetting: Theoretically the addition of sodium sulfate to the synthetic detergent should materially

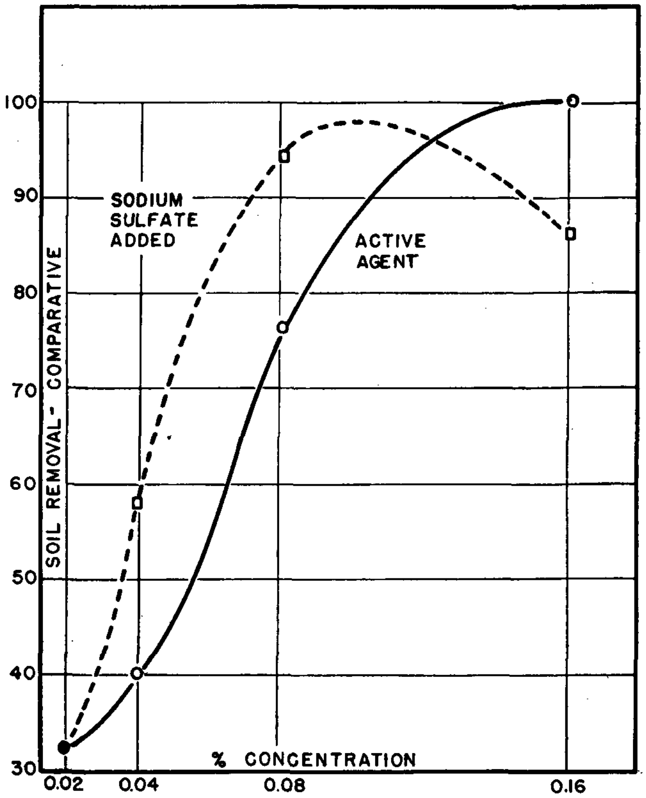

Fig. 3. Effect of sodium sulfate on detergency.
Sufficient sodium sulfate added in the one case to provide a solution concentration of 0.2%.

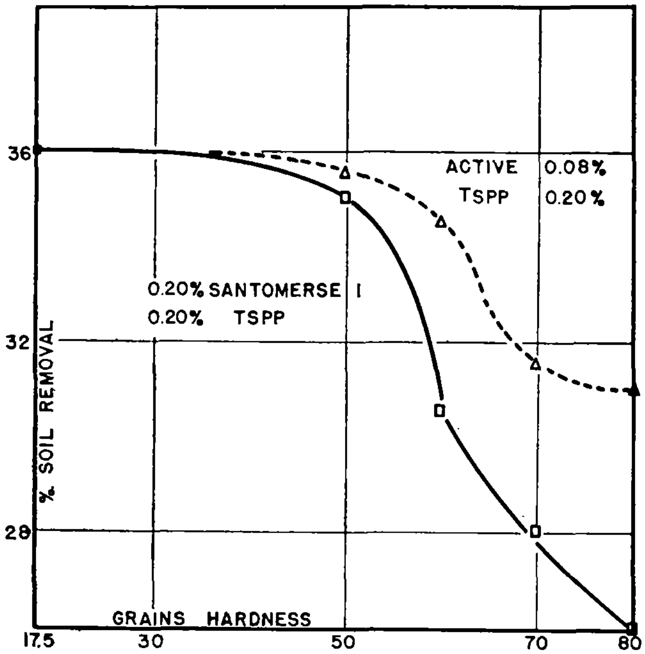

FIG. 4. Effect of electrolyte upon hard water detergency. Active and TSPP in one case, and active, TSPP, and sodium sulfate in the other.

enhance wetting. Tests were made utilizing the canvas disc method (1 inch No. 6 Mt. Vernon duck) in which Santomerse No. 1 (40% active) was compared with the pure product. Reference to Fig. 1 will show the effectiveness of dilution with sodium sulfate. For example, a 10-second wetting time can be obtained with 0.14% of material containing sodium sulfate and 0.18% of pure material. On the basis of active agent this represents 0.056% vs. 0.18%, or a 69% reduction in the amount of active agent necessary when sodium sulfate is used. The slower wetting times show lower differentials, but theory and practice are the same.

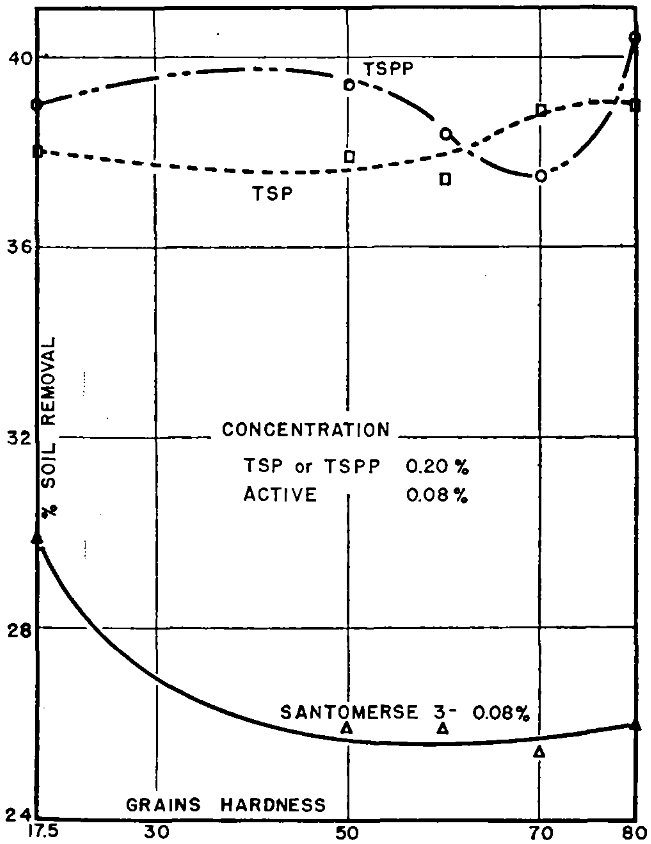

FIG. 5. Effect of electrolyte upon hard water detergency. Active combined with either TSP or TSPP.

Detergency: The method used for the detergent tests which follow have been adequately described elsewhere (13).

Cation effect upon detergency is clearly shown in Fig. 2 in which values greater than those obtained with the pure compound result when an optimum conversion to the magnesium salt is maintained, with resultant reduction in efficiency by excess ion.

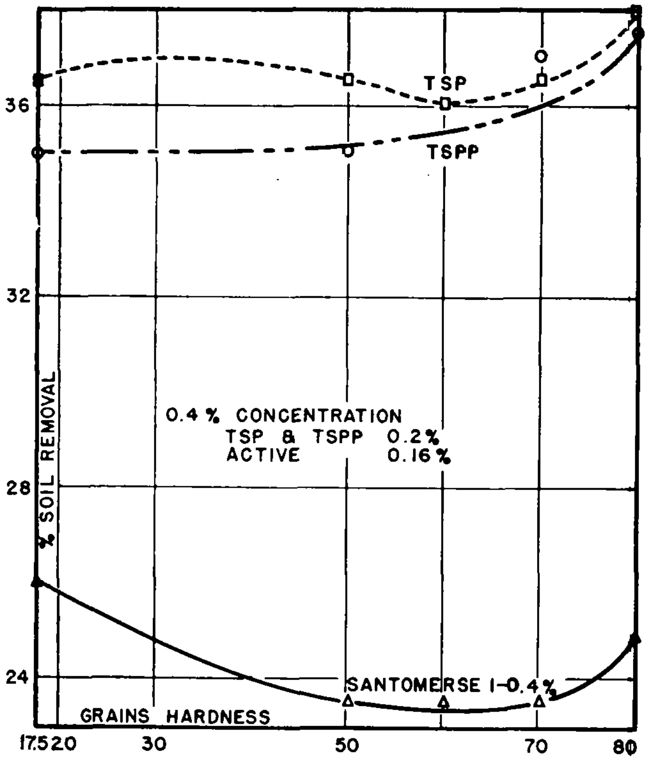

FIG. 6. Effect of electrolyte upon hard water detergency. 0.4% total concentration.

The curves of Fig. 3 show that the addition of sodium sulfate up to a given concentration increases detergent efficiency (reduces the amount of active required) but that, above an optimum concentration, increase in electrolyte results in lowered detersive efficiency. Since these tests were made in 300 p.p.m. hard water (hardness 60%-Ca-40% Mg), it is probable that results with electrolyte would not drop off as sharply at higher active ingredient concentrations.

The next series of tests shows the effect of extremely hard water upon two systems, one comprising pure detergent combined with TSPP, and the other a combination of the equivalent amount of active ingredient to which has been added sodium sulfate and TSPP, the latter material in the same amounts in both series of tests. The curves of Fig. 4 show that, as with Fig. 3, the optimum detergent results were obtained at 17½ grains (300 p.p.m.) hardness, but that the added electrolyte definitely reduced efficiency at the higher water hardnesses.

Fig. 5 demonstrates that the addition of either TSP or TSPP markedly improved detergent efficiency over

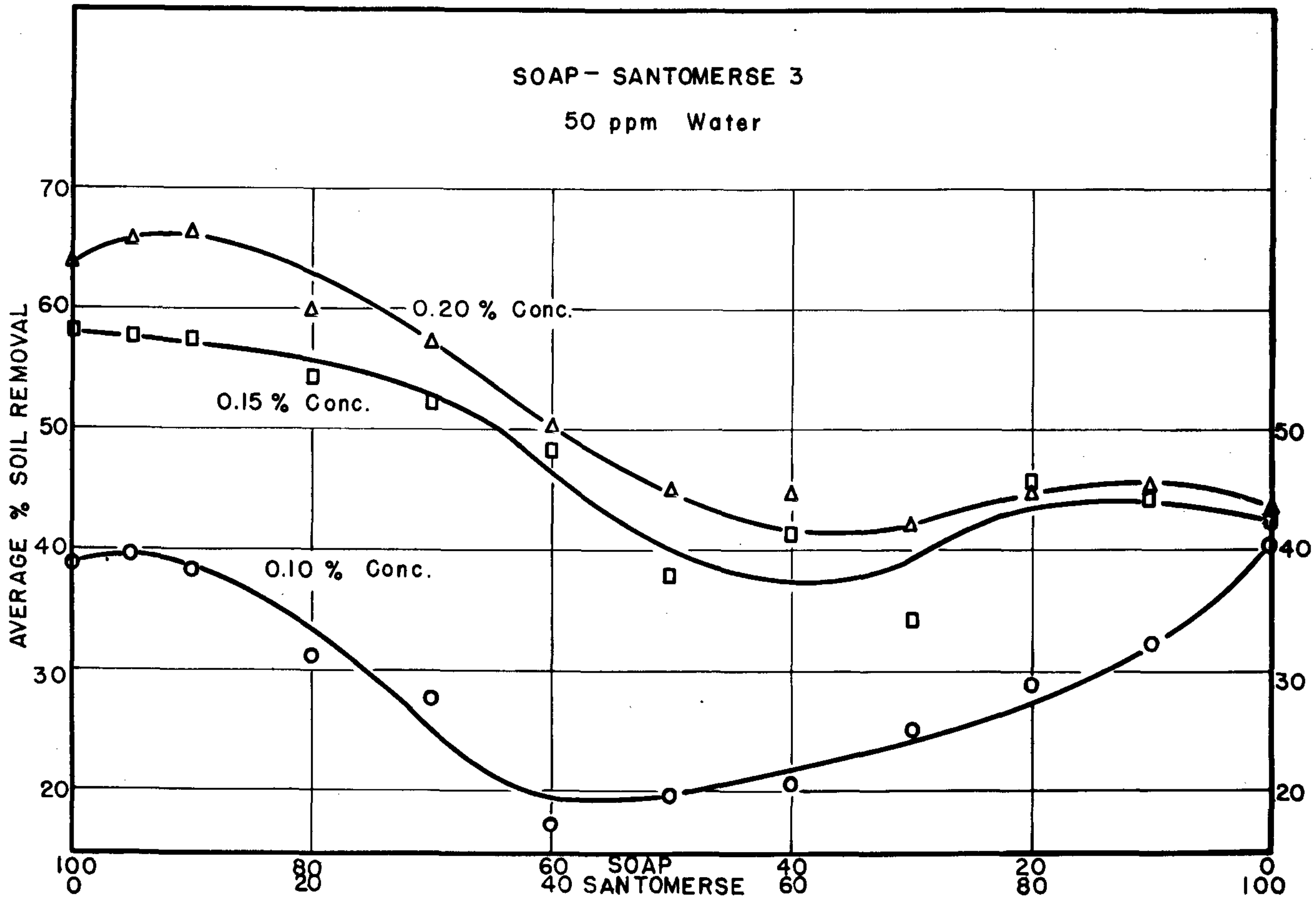

FIG. 7. Detergency of soap-Santomerse No. 3 combinations. 50 p.p.m. soft water.

LATHER AND pH DATA

% Soap	% Merse	0.10% Conc.		0.15% Conc.		0.20% Conc.	
		pH	Suds	pH	Suds	pH	Suds
100	0	9.6	¼″	10.1	4″	10.1	4″
95	5	9.6	⅛″	9.8	4″	10.1	4″
90	10	9.5	tr.″	9.7	4″	10.0	4″
80	20	9.2	tr.″	9.5	4″	9.7	4″
70	30	9.0	tr.″	9.2	4″	9.5	4″
60	40	8.7	tr.″	9.0	1″	9.4	4″
50	50	8.2	tr.″	8.5	1″	8.9	4″
40	60	7.9	⅛″	8.1	1″	8.5	4″
30	70	7.6	½″	7.9	1″	8.2	4″
20	80	7.3	2″	7.5	2″	7.8	4″
10	90	7.0	2″	7.2	2″	7.3	4″
0	100	6.3	4″	6.2	4″	6.1	4″

the water hardness range. This may be attributed at least in part to water softening, but even at lower water hardnesses the effect of electrolyte builders is marked. The same generalizations may be applied to the data of Fig. 6, except that the over-all detergency is lower, and this lowered detergency again may be attributed to excess of electrolyte over the optimum value. The improvement in detergency of combinations containing TSP or TSPP may be attributed to the synergistic action of these materials due in part to the fact that they are water softeners and mild detergents in their own right, but neither action satisfactorily explains the marked increase in detergency which may be attributed to the valency of the orthophosphate and pyrophosphate ions.

Soap Combinations: Soap is an excellent electrolyte, and as such it might be expected that some of the effects produced by the alkaline electrolytes might also be true of its use in combination with a synthetic detergent.

Figs. 7 and 8 show graphically the results with pure synthetic and a pure soap (medium titer), and their various combinations. It is interesting to note that water hardness (from 50 p.p.m. to 300 p.p.m.) improves the detergent efficiency of the synthetic product when used alone, which would be expected according to previous results and theory. It cannot be said that the alkyl benzene sulfonate is a good soap builder or that soap is an effective builder for the synthetic. Only under optimum solution concentration conditions does the synthetic produce a relatively minor increase in detergency.

Figs. 9 and 10 show that Santomerse No. 1 (containing sodium sulfate) is an even poorer soap builder than the pure synthetic. This possibility might have been expected in view of the results obtained with Santomerse No. 1 when an excess of electrolyte is present.

Although Santomerse does not act as a soap builder in the usual sense in the lower solution concentrations, this may be attributed to incompatibility (actually to acid decomposition of the soap), as evidenced by the fact that pH values at the detergent minima are below that for normal soap and lather values are also at a minimum at the same point.

However, soap and Santomerse compositions have been used extensively and successfully by the armed services, but in these cases the solution concentrations were relatively high. The Bureau of Ships (14) found these compositions useful not only in soft or extremely hard water but in sea water as well. The combinations provided a suitable physical state for use and when in sufficient concentration resulted in excellent detergent results (13). The fact that reduction in size of the alkyl side chain of the alkyl benzene sulfonate resulted in improved soap compositions in hard water has been demonstrated (16). A further variation may be expected in the effect upon surface activity attained by change in side chain length of the alkyl benzene sulfonate. No attempt has as yet been made to investigate this phase of the problem.

Other investigators (4) have demonstrated that lather minima occur with soap and other synthetic detergents but did not determine whether an actual detergent drop occurred at the same point.

Bentonite: Bentonitic materials have been shown as possessing detergent value. They are non-caking themselves and actually exert anti-caking characteristics as adjuncts to Santomerse No. 1 to prevent it from caking under the extremely adverse storage conditions of high temperature and high humidity (under which conditions an inhibitor is necessary). The detergent activity of such compositions was tested. The bentonites chosen for detergent test work were representative of three generally varying types, chosen by evaluation of their pH, dispersion, and methylene blue adsorption values. These values, given in Table III, were developed, using the following tests.

Methylene blue adsorption was used (16) as one means for the evaluation of surface activity. The

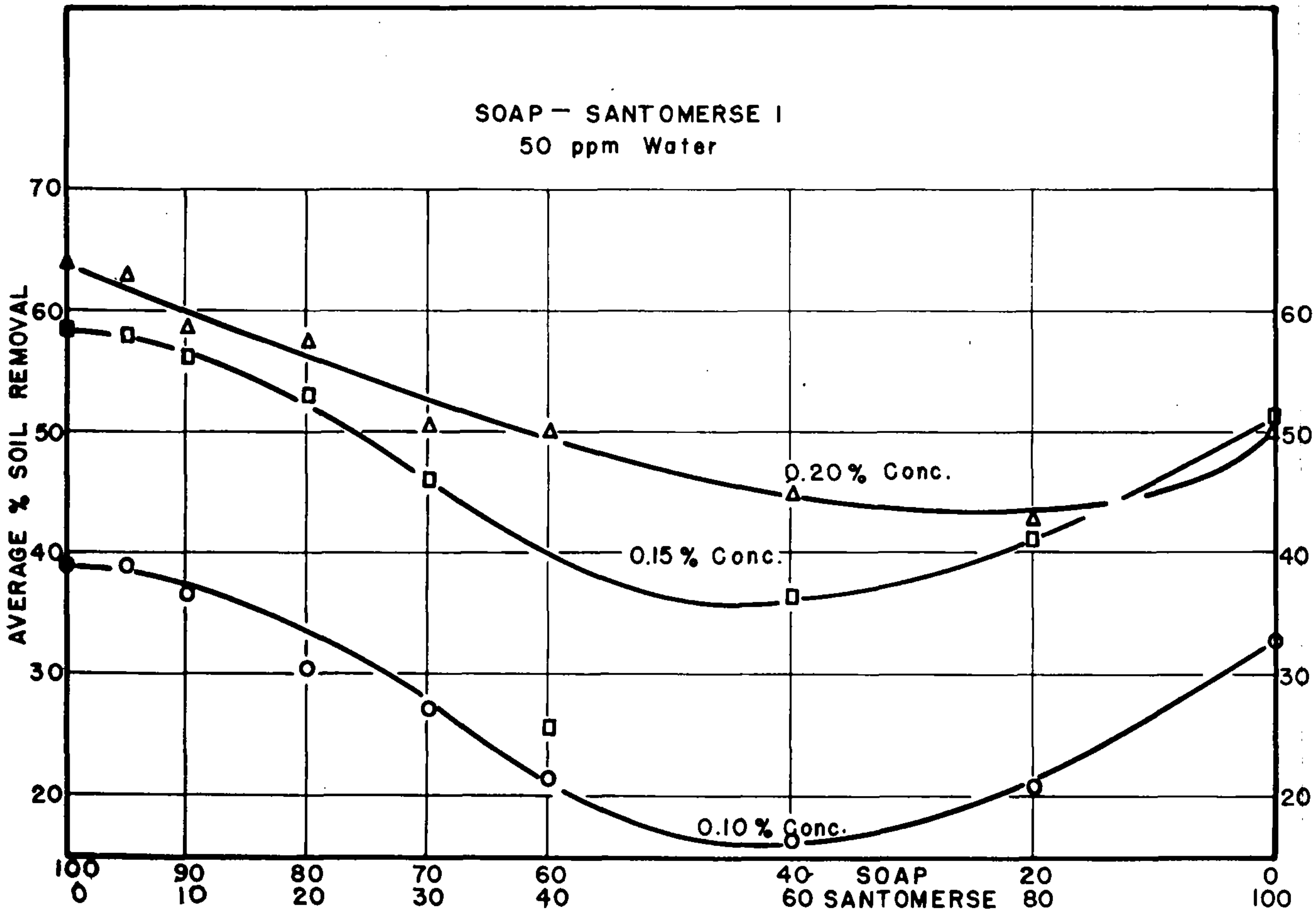

FIG. 9. Detergency of soap-Santomerse No. 1 combinations. 50 p.p.m. soft water.

LATHER AND pH DATA

% Soap	% Merse	0.10% Conc.		0.15% Conc.		0.20% Conc.	
		pH	Suds	pH	Suds	pH	Suds
100	0	9.6	¼"	10.1	4"	10.1	4"
95	5	9.5	tr."	9.9	4"	10.0	4"
90	10	9.4	tr."	9.8	4"	9.9	4"
80	20	9.0	tr."	9.5	4"	9.8	4"
70	30	8.7	tr."	9.3	2"	9.6	4"
60	40	8.3	tr."	9.1	¼"	9.3	4"
40	60	7.9	tr."	8.4	¼"	8.6	1"
20	80	7.4	⅛"	7.6	¼"	7.7	1"
0	100	6.4	2"	6.8	4"	6.8	4"

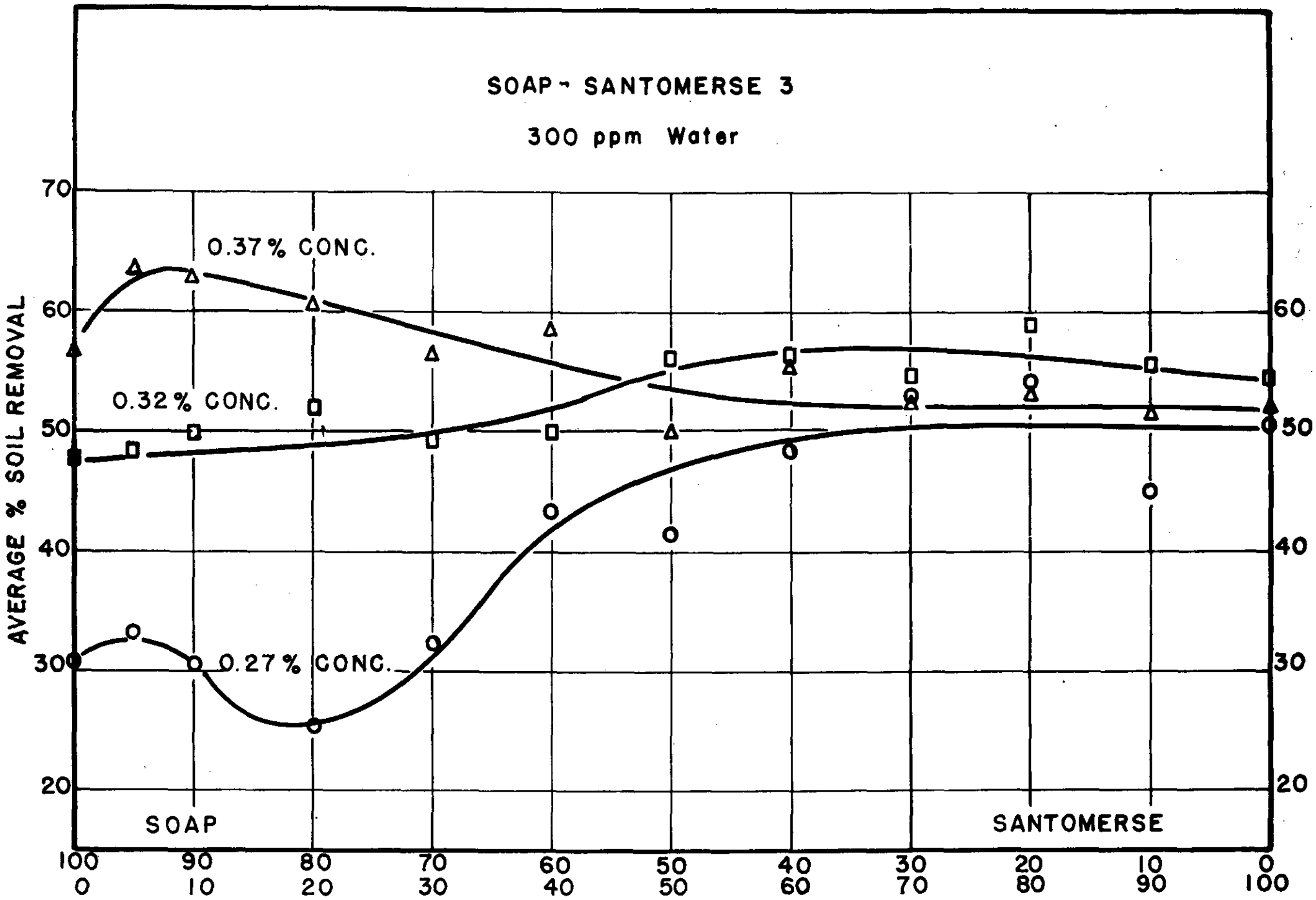

FIG. 8. Detergency of soap-Santomerse No. 3 combinations. 300 p.p.m. hard water.

LATHER AND pH DATA

% Soap	% Merse	0.27% Conc.		0.32% Conc.		0.37% Conc.	
		pH	Suds	pH	Suds	pH	Suds
100	0	9.4	tr"	9.8	1"	9.8	4"
95	5	9.3	tr"	9.4	½"	9.7	4"
90	10	9.2	tr"	9.3	¼"	9.5	4"
80	20	8.9	tr"	9.1	¼"	9.3	4"
70	30	8.6	⅛"	8.7	1"	9.0	4"
60	40	8.3	½"	8.5	2"	8.8	4"
50	50	7.8	4"	8.1	4"	8.4	4"
40	60	7.6	4"	7.8	4"	8.1	4"
30	70	7.4	4"	7.5	4"	7.7	4"
20	80	7.3	4"	7.4	4"	7.5	4"
10	90	7.1	4"	7.3	4"	7.3	4"
0	100	6.1	4"	6.8	4"	6.3	4"

present test was developed to provide a comparative evaluation of the bentonite samples.

Adsorption Values: The technic used follows:

1. Prepare a 2.0% solution (by weight) of methylene blue.
2. Disperse 10.0 g. of bentonite in 490 ml. of distilled water using the Waring Blendor.
3. To 50 g. quantities of freshly agitated bentonite-water dispersion add given aliquots (by weight) of methylene blue solution.

TABLE III.

Bentonite Evaluation.

Bentonite	pH 1% dispersion	Dispersion mls. solid settled out	Adsorption value (mgs. methylene blue/gm. bentonite)
A	9.40	1.5	300
B	4.05	3.0	80
C	7.10	7.0	160

4. Vigorously stir the mixture by hand.
5. Filter on a Buchner funnel, using two thicknesses of No. 1 Whatman filter paper.
6. Discard the initial 5-10 ml. through the funnel and collect 15-20 ml. of the subsequent filtrate in a test tube. If the filtrate is deeply colored, decrease the volume of methylene blue solution used. (Note: If too dilute a concentration of methylene blue solution is used, the test is inoperative.)
7. The test is considered as complete when a 2.5 g. addition of methylene blue solution just produced a clear filtrate. (Note: Wet the filter paper with water and confine the coagulated mass to the center of the filter. In most cases when the coagulation was complete, the dispersion was quite viscous.)
8. Calculate and record the maximum number of milligrams of methylene blue adsorbed per gram of bentonite.

Dispersion Tests: Two grams (2.0 g.) of the bentonite sample were added gradually and with stirring to 98 ml. of distilled water in a 100- ml. graduated cylinder. The cylinders were stoppered and shaken thoroughly prior to letting them age for 24 hours. At the end of this aging period, the cylinders were examined for volume of sediment and the apparent degree of dispersion, evident from the appearance of the dispersed samples. The results of this test are shown in Table III.

pH Values: A 1.0% dispersion of bentonite was made in freshly boiled, distilled water. Measurements were made at 25±1°C. using a Beckman meter and appropriate glass electrode.

Reference to Fig. 11 shows that only sample C, the intermediate bentonite, appears to provide synergistic effect combined with Santomerse No. 1 at a 90% Santomerse No. 1 content. The other samples and compositions indicate only that bentonite acts as a diluent. The diluent effect is substantiated in hard water (Fig. 12) without exhibiting any synergistic action.

Discussion

Builders for soaps comprise electrolytes, more generally the alkaline ones, since soap is acid-sensitive. Less well known are the effects of the relatively neutral electrolytes such as sodium chloride or sodium sulfate which are generally considered as diluents. The amounts of these agents which can be used with soap are comparatively low since decrease in surface activity results after only minor percentages of them have been added.

Builders for synthetic detergents have not been well understood, and in many cases sodium chloride, sodium sulfate and other electrolytes are considered solely as make-weights and concomitant to the manufacture of the synthetic. It should be recognized however, that many of the pure or salt-free detergents possess the undesirable characteristics of hygroscopicity, color, waxiness, or other undesirable features.

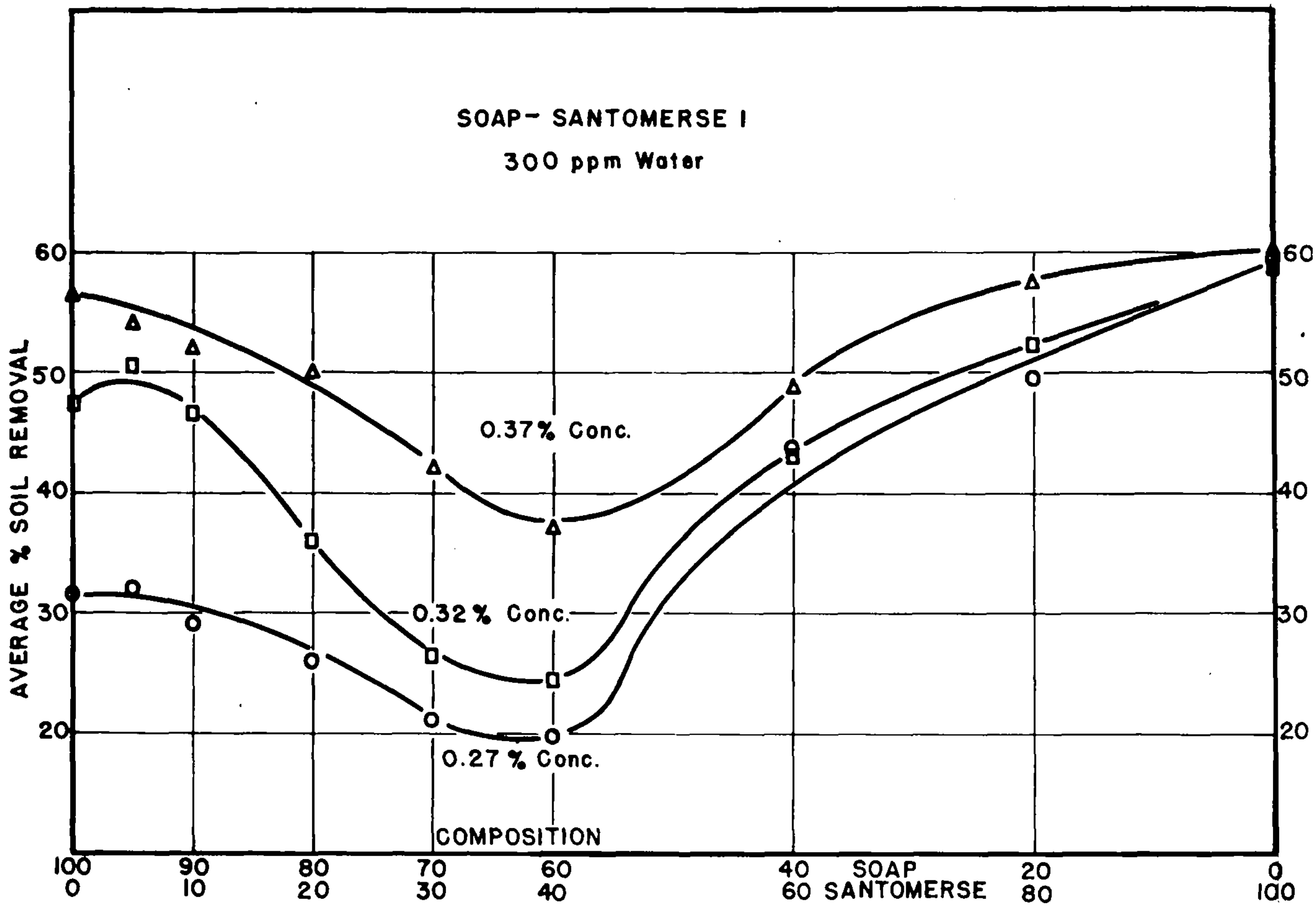

FIG. 10. Detergency of soap-Santomerse No. 1 combinations. 300 p.p.m. hard water.

LATHER AND pH DATA

% Soap	% Merse	0.27% Conc.		0.32% Conc.		0.37% Conc.	
		pH	Suds	pH	Suds	pH	Suds
100	0	9.4	tr."	9.8	1"	9.8	4"
95	5	9.3	tr."	9.7	⅛"	9.7	4"
90	10	9.2	tr."	9.6	⅛"	9.6	4"
80	20	8.7	tr."	9.2	⅛"	9.4	¼"
70	30	8.4	tr."	8.8	tr."	9.0	⅛"
60	40	8.1	tr."	8.4		8.6	⅛"
40	60	7.7	⅛"	7.8	¼"	8.1	¼"
20	80	7.3	1"	7.4	1"	7.3	4"
0	100	6.4	4"	6.4	4"	6.4	4"

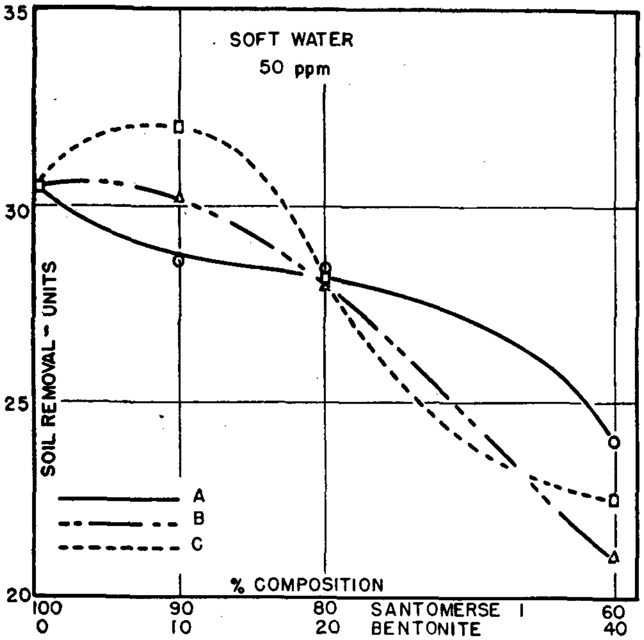

FIG. 11. Detergency of Santomerse No. 1-bentonite mixtures. 50 p.p.m. soft water.

LATHER AND pH DATA

Sample	% Composition							
	100		90-10		80-20		60-40	
	pH	Suds	pH	Suds	pH	Suds	pH	Suds
Santomerse No. 1	5.7	4	....	....	....	....	....	....
Bentonite A	....	....	6.0	3½	6.2	3½	6.4	3½
Bentonite B	....	....	5.0	4	4.7	4	4.45	2
Bentonite C	....	....	6.0	3½	6.0	3½	6.1	3½

Certain synthetic detergents can be manufactured in the salt-free state since there is demand for materials soluble in non-aqueous solvents or in which freedom from salt is required, because of the undesirable effect of electrolyte upon the end-product of usage. However, this purification generally entails added operations which increase cost. Consequently lower cost, improved surface activity and physical characteristics often result by building the active ingredient.

Chemical methods for analysis of the synthetic detergents have often been resorted to as a means for evaluation. A more effective method, especially in the absence of practical information as to effectiveness, is subjection to especially devised tests which comparatively evaluate the materials under conditions approaching plant operation. The latter method is especially valuable when several products of unknown characteristics and varying active ingredient content are to be evaluated. Equal amounts of active ingredient in two distinct types of synthetic detergent will not necessarily produce equivalent performance.

The foregoing data for alkyl benzene sulfonate agree well with theory and indicate both the suitability and desirability of "building" synthetic detergents: Type of builder and amount will be determined by conditions of usage.

Summary

A theory to account for synergistic action of electrolytes with soap and synthetic detergents is reviewed.

The effect of electrolyte builders upon the surface activity of pure and electrolyte-built dodecyl benzene sodium sulfonate is described for the following characteristics: lather, surface and interfacial tension, wetting, and detergency.

Lather is improved by the addition of electrolytes such as sodium sulfate or magnesium chloride, but a decrease results after optimum amounts are added. Lesser amounts of bivalent cations are required for optimum results than for monovalent materials.

Surface and interfacial tension values are lowered by either neutral or alkaline electrolytes. The greater the valency of anion, the less the amounts of electrolyte required, but the sooner the optimum values are reached and passed.

Wetting results can be improved up to 69% by the addition of electrolyte to pure active ingredient.

Detergency is improved by the addition of electrolyte, sodium sulfate being quite effective, but alkaline salts improve it even more, the valency of the anion appearing to exert the greatest influence.

Combinations of soap and alkyl benzene sulfonate tested in low solution concentration show synergistic action in only one of six cases whereas all show distinct detergent minima, corresponding to a point where lather is at a minimum and pH values drop below that for soap alone. Presence of sodium sulfate tends to reduce the detergency of the soap-synthetic mixtures though the effect of electrolyte in improving detergency of the synthetic agent (apart from soap) is indicated. It is known that soap-synthetic detergent combinations have been used suc-

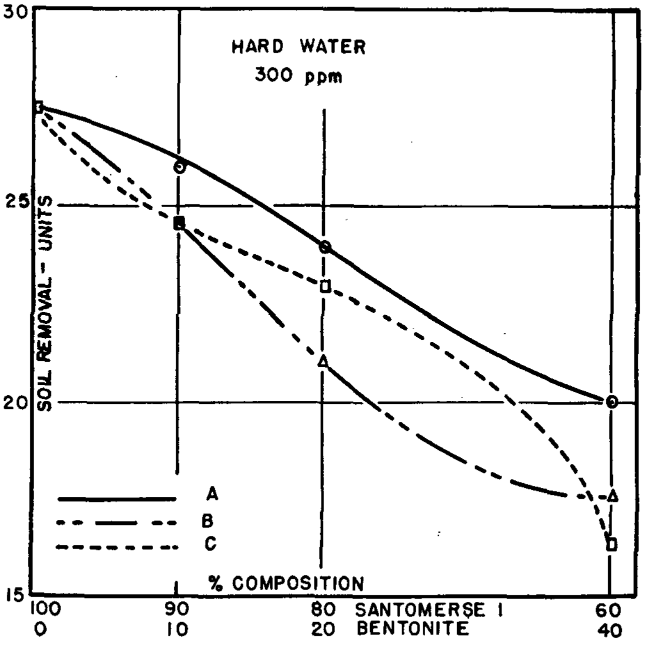

FIG. 12. Detergency of Santomerse No. 1-bentonite mixtures. 300 p.p.m. hard water.

LATHER AND pH DATA

Sample	% Composition							
	100		90-10		80-20		60-40	
	pH	Suds	pH	Suds	pH	Suds	pH	Suds
Santomerse No. 1	5.8	4	....	....	....	....	....	....
Bentonite A	....	....	6.0	3	6.2	3	6.3	¾
Bentonite B	....	....	5.0	4	4.7	3½	4.3	¾
Bentonite C	....	....	5.9	3½	6.0	3½	6.1	¾

cessfully by the armed forces. The condition which favored such use was high solution concentration.

No general improvement in detergency was attained by addition of the excellent caking inhibitor, bentonite, to the sulfate-built detergent.

Acknowledgment

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Improvement of Keeping Quality of Edible Fats by Some Commercially Available Tannins*†

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AS revealed by the number of publications in recent years, a great deal of effort has been expended in research work toward the development of suitable antioxidants and synergistic combinations to be added to fats and oils. Several years ago the study of tannins for the purpose of improving the keeping quality of fats was begun in this laboratory. Tannins were selected for investigation because of their wide occurrence in foods (1) and because their chemical structures suggested antioxidant properties.

A search of the literature at that time revealed little or no data on tannins as antioxidants. Lea (2) has two notes of some interest in his book "Rancidity in Edible Fats." On page 167 he states "substances insoluble in fat-solvents or decomposed by alkali, e.g., proteins, tannins, glucosides or carbohydrates may, perhaps, also assist in protecting fats in the tissue." On page 171 the statement is made that "Chevreul (1856) was familiar with the fact that oak and certain other woods delayed the drying of linseed oil and that American Indians are said to have used the bark of trees for retarding the development of rancidity of bear grease."

Moureu and Dufraisse (3) included tannic acid in a group of substances which tended to retard oxidation changes of another group of organic substances which were relatively easily oxidized and which included fats.

Olcott and Matill (4) listed tannic acid with the "inactive compounds" when tested on crude esters of hydrogenated cottonseed oil. A footnote explained that some of the substances in this "inactive list," when added at levels of 0.02% and 0.1%, exhibited slight antioxygenic activity. Some of the substances in this table were specifically mentioned as possessing slight antioxidant effect, but tannic acid was not included.

Von H. Schönfeld (5) lists concentrated tannin as an agent for removing mucilage from fats. Later Musher (6) claims the use of gallotannin in treatment of paper so as to retard rancidity. Musher (7) and Verbeek (8) in patents which were pending at the same time presented data showing that tannic acid can be added directly to fats to retard the development of rancidity. Musher showed that 50 P.P.M. of tannic acid, when added to lard, increases the keeping quality from two hours by the active oxygen method to six hours. Verbeek showed that when 50 P.P.M. of tannic acid was suspended in oleo oil, the keeping quality was increased from eight hours to 15. Musher was primarily concerned with the enhanced effect resulting from heating the tannin and fat to a temperature "over 250°F." Verbeek was primarily concerned with the improvement of the keeping quality of fats by a treatment with tannins in which the tannins and a tannin compound were removed, as by filtration.

This paper presents data on the process of improving the quality of fats and consists of bringing into contact with relatively dry fat (containing less than 0.2% moisture) a dry tannin material (usually containing less than 12% moisture) and then removing the tannin and tannin complex by filtration. It also shows the effect of varying the temperature of treatment and how this variable is related to Musher's patent.

Experimental

A—Methods

(1) Standardized Procedure for Treatment of Fats With Tannin: Three hundred grams of fat are weighed into a 500-ml. wide-mouth Erlenmeyer flask and heated on an electric hot plate to 160°F. while being stirred with an electric agitator. 0.300 ± .001 gm. of the tannin is added and the stirring continued for 14 minutes. The temperature is held at 160°F. ± 5°F. throughout the process. 0.5 gram of Dicalite Speedplus (commercial grade of diatomaceous earth) is added and stirring is continued for one more minute. The fat is filtered through a Whatman No. 4 filter paper. The tannin and Speed-

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*A paper presented at the A.O.C.S. Fall Convention at Chicago, Nov. 7-9, 1945.

†Part of the data were presented at the Conference on Problems Related to Fat Deterioration in Foods under the auspices of Committee of Food Research, Research and Development Branch, Military Training Division, Office of The Quartermaster General in Washington in June 1945.