Summary

Hydrogen transfer catalysts are known to promote the elaidinization and conjugation of unsaturated fatty acid derivatives. More extensive reactions were indicated when palladium was tried as a polymerization catalyst. A subsequent study showed that methyl linoleate could be readily cyclized and aromatized in the presence of palladium.

Methyl linoleate was heated in an evacuated ampule for 6 hrs. at 270°C. with 5% of a 10% palladium on charcoal. The iodine value was lowered to 43.9 and the apparent linoleate content to less than 2%. The products were separated by urea segregation and distillation. They consisted of approximately 7% polymer, 18% methyl stearate, 40% mono-olefins, and 30% of a methyl ester of an aromatic fatty acid (handling loss 5%). The aromatic material was readily oxidized to orthophthalic acid.

The mechanism by which aromatics, mono-olefins, and saturates are produced through cyclization and hydrogen transfer is not known, but possible routes are suggested.

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An Investigation of the Adsorption of Detergent and Builders Onto Cotton and Soil by Radiotracer Methods

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THE FACT THAT ANIONIC DETERGENTS are adsorbed onto textile fibers from aqueous solutions has been demonstrated by many studies, such as those of Neville and Harris (1), Neville and Jeanson (2), Gardiner and Smith (3), Aickin (4), Swanston and Palmer (5), and Flett, Hoyt, and Walter (6). Harris has published an excellent review of the adsorption of surface-active agents by fibers (7). That adsorption onto fibers does take place is not surprising since adsorption at interfaces is a manifestation of the surface-active properties of long-chain ions. Thus the lowering of surface tension, wetting and spreading action, foaming, emulsification, and peptization all involve adsorption of long-chain ions or aggregates of these ions at interfaces.

The effect of alkaline builders on the surface-active properties of typical detergents has been the subject of much research activity; for example, Harris (8), Merrill and Getty (9), Niven and Gadberry (10), and Morrisoe and Newhall (11) have shown that builders markedly enhance the surface activity of dilute synthetic detergent solutions and also improve detergent action, in a synergistic fashion, especially with polyphosphates. In order to utilize this synergistic behavior, commercial laundry materials are heavily built with alkaline salts. Molecularly dehydrated phosphates are widely used in formulations designed as cotton detergents. In view of the known adsorption of detergents onto textile fabrics and synergistic effects of builders in detergency, an exploratory study was made on the effect of various builders on the adsorption of a long-chain alkylbenzene sulfonate on cotton and soils. A study was also made of the adsorption of builders on cotton and soils. With one exception the adsorption was determined by means of radioactive techniques. The purpose of this study was to obtain data which might help explain the mechanism by which builders improve detergent action.

Materials and Reagents

Preparation of Radioactive Dodecyl Benzene Sulfonate. Radioactive dodecyl benzene sodium sulfonate, containing S^{35}, was synthesized in the following manner. Some 29 ml. of technical dodecyl benzene, b.p. 60–160°C. (0.3 mm.) were placed in a 3-neck flask fitted with thermometer, stirrer, and dropping funnel. The contents were cooled by partially immersing in ice water. Five ml. of freshly fumed sulfuric acid, containing the desired activity of S^{35} as sulfuric acid, was added to a mixture of 15 ml. of sulfuric acid (100%) and 4 ml. of fuming sulfuric acid (30%). The acid mixture, after being cooled in an ice bath, was added dropwise with continuous stirring over a half-hour period to the dodecyl benzene in the cooled flask. The ice water was replaced by a constant temperature bath at 40 ± 1°C., and stirring was continued for 2 to 2½ hours. The sulfonation mixture was transferred to an 800-ml. beaker, the flask was rinsed twice with 10 ml. of water, and rinsing was completed with 300 ml. of 95% ethanol. The alcoholic sulfonation mixture was then neutralized to a pH of 7–7.2 with sodium hydroxide solution (40%). The neutralized mixture was allowed to stand for 1 hr. to permit salts to settle and then was filtered through a Buchner funnel, using No. 40 Whatman paper. The residue was washed twice with 50-ml. portions of 95% ethanol. The filtrate was extracted three times with 50-ml. portions of petroleum ether to remove unreacted dodecyl benzene and then was evaporated on a steam bath. The residue was transferred to an oven and dried for 3–4 hrs. at 105°C. The residue was dissolved in absolute alcohol, and the solution was filtered and evaporated on a steam bath. The residue was dried for 3–4 hrs. at 105°C. and overnight over phosphorus pentoxide. The detergent had a specific activity of 0.1 microcurie/mg. Its sulfur content was 9.05% compared to the calculated value of 9.19% for dodecyl benzene sodium sulfonate. A stock solution

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was prepared by dissolving 1 g. of the synthesized detergent in 1,000 ml. of distilled water. The pH, which was nearly neutral, was adjusted to exactly 7.0.

Non-radioactive sodium dodecyl benzene sulfonate was similarly prepared. Bleached, desized Indian Head cotton fabric (Nashua Mills Manufacturing Company), 48 x 54 thread count, 5 oz. per square yard, was cut into circles approximately 1¾ in. in diameter for adsorption tests. The cloth was desized with caustic scour and soap solution, followed by repeated rinsings, until all soap was removed. Soil constituents as shown in Table I were used in adsorption tests. The particle sizes and percents given were estimated from microscopic examination. Stock solutions of radioactive builders were prepared as follows:

TABLE I
Soil Constituents

	Particle size in microns	Percentage
Lampblack, Federal Specification TT-L-70, Monsanto Chemical	0.7–1.5	60
	0.7	40
Magnetite (Fe_3O_4), Raven Black, C. K. Williams	1.0–1.5	10
	1.0	80
	0.5	10
Ferric Oxide (Fe_2O_3), Red N-1860, C. K. Williams	15	20
	15	30
	8	10
	5	10
	2	30
Pulverized Silica (through 20 mesh)	27	58
	12–27	30
	2–12	10
	2	2
Iron, Baker's (by hydrogen reduction)	30	38
	30	30
	14	20
	2–7	10
	2	2

Sodium Sulfate ($Na_2S^{35}O_4$). Dilute radioactive sulfuric acid was added to sodium sulfate solution, and the solution was adjusted to the neutral point.

Sodium Carbonate ($Na_2C^{14}O_3$). Radioactive sodium bicarbonate solution was added to sodium carbonate, and the solution was titrated with sodium hydroxide to the correct pH for sodium carbonate.

Preparation of Radioactive Sodium Phosphates

Trisodium Phosphate ($Na_3P^{32}O_4$). 83.3 ml. of 85% phosphoric acid solution were diluted to one liter with distilled water. A 10-ml. aliquot was taken and diluted to about 100 ml. Radioactive phosphoric acid was added. A solution of sodium hydroxide, approximately 1.0N, was prepared and standardized. A calculated amount of the sodium hydroxide solution was added to make trisodium phosphate (Na_3PO_4), and the solution was diluted to 730 ml. with distilled water.

Tetrasodium Pyrophosphate ($Na_4P_2{}^{32}O_7$). 83.3 ml. of 85% phosphoric acid solution was diluted to one liter with distilled water. A 23.1-ml. aliquot was taken and diluted to about 100 ml. Radioactive phosphoric acid was added. A solution of sodium hydroxide, approximately 1N, was prepared and standardized. A calculated amount of the sodium hydroxide solution was added to make disodium hydrogen phosphate. The phosphate solution was evaporated to a small volume and transferred to a platinum dish. The solution was evaporated to dryness and dehydrated over a Fisher burner and then heated in a furnace at 985°C. for 1 hr.

Sodium Tripolyphosphate ($Na_5P_3{}^{32}O_{10}$). 2.0 g. of radioactive disodium hydrogen phosphate, prepared as described above, was mixed well with 0.85 g. of unadjusted Calgon in a platinum dish. Calgon corresponds closely to sodium metaphosphate $(NaPO_3)_6$. The mixture was heated to 900°C. and cooled slowly in a furnace to 550°C., over a period of at least an hour. The melt was removed from the furnace and allowed to cool to room temperature.

TABLE II
Relative Adsorption of Detergent on Cotton from Solution Containing Various Builders

Builder concentration molar in (Na)+ x 1,000	Sodium chloride		Sodium sulfate		Sodium carbonate		Trisodium phosphate		Sodium pyrophosphate		Sodium Tripolyphosphate	
	pH	Relative adsorption	pH	Relative adsorption	pH	Relative adsorption	pH	Relative adsorption	pH	Relative adsorption	pH	Relative adsorption
0.01% Detergent Concentration												
....	7.0	100	7.0	100	7.0	100	7.0	100	7.0	100	7.0	100
1	7.0	102	7.1	100	10.5	89	10.4	96	9.8	78	10.0	81
2	6.9	103	6.9	100	10.6	89	10.7	91	10.1	62	10.1	66
4	6.9	108	6.9	99	10.8	91	11.0	91	10.2	52	10.1	54
10	6.9	112	6.9	99	10.9	91	11.3	91	10.4	59	10.1	61
20	6.9	110	6.9	101	11.1	91	11.5	92	10.5	62	10.2	75
0.05% Detergent Concentration												
....	7.0	100	7.0	100	7.0	100	7.0	100	7.0	100	7.0	100
1	7.0	99	7.0	99	10.6	91	10.6	97	9.8	85	9.7	89
2	6.9	102	7.0	102	10.7	90	10.9	94	10.0	66	9.9	72
4	6.8	101	7.0	101	10.8	89	11.1	89	10.1	56	10.0	57
10	6.8	99	6.9	93	11.0	90	11.6	78	10.4	59	10.2	53
20	6.8	99	6.9	94	11.1	85	11.8	74	10.4	65	10.3	59
0.10% Detergent Concentration												
....	7.0	100	7.0	100	7.0	100	7.0	100	7.0	100	7.0	100
1	7.0	97	7.0	95	10.2	95	10.4	94	9.6	92	9.4	87
2	7.0	97	7.0	92	10.4	93	10.5	89	9.8	73	9.7	77
4	7.0	98	7.0	91	10.5	84	10.8	88	10.0	57	9.7	53
10	6.9	96	6.9	87	10.7	75	11.4	79	10.0	63	9.7	58
20	6.9	95	6.9	90	10.8	77	11.5	75	10.1	63	9.8	59
0.15% Detergent Concentration												
....	7.0	100	7.0	100	7.0	100	7.0	100	7.0	100	7.0	100
1	6.9	102	7.0	90	10.5	88	10.1	92	9.6	84	9.6	88
2	6.9	101	7.0	91	10.7	85	10.3	89	9.8	72	9.8	79
4	6.9	101	7.0	89	10.8	81	10.9	86	9.9	64	10.0	64
10	6.9	98	6.8	90	11.0	77	11.2	85	10.2	70	10.1	62
20	6.9	103	6.8	91	11.2	77	11.5	84	10.2	75	10.1	61

Non-radioactive solutions of the above builders and

TABLE III

Relative Adsorption of Detergent from Solutions [a] Containing Various Builders at Same Anionic Concentration

	Concentration of builder molar in anion	Relative adsorption soil A			Soil B	Cotton cloth
		Run 1	Run 2	Run 3		
None	....	100	100	100	100	100
Sodium chloride	4 x 10^{-3} (Cl)	79	75	80	....	105
Sodium sulfate	4 x 10^{-3} $(SO_4)^{-2}$	65	65	72	....	92
Sodium carbonate	4 x 10^{-3} $(CO_3)^{-2}$	29	35	33	....	83
Trisodium phosphate	4 x 10^{-3} $(PO_4)^{-3}$	12	11	14	62	74
Tetrasodium pyrophosphate	4 x 10^{-3} $(PO_4)^{-3}$	8	8	7	57	60
Sodium tripolyphosphate	4 x 10^{-3} $(PO_4)^{-3}$	8	8	7	58	58

[a] 0.1% sodium dodecyl benzene sulfonate.

sodium chloride were also prepared. The Calgon was of commercial grade. Other reagents were C.P. grade. Radioactivity of samples was determined in a windowless flow counter, Radiation Counter Laboratories, RCL Mark 12, Model 1, in the proportional region, using methane gas.

Procedures and Results

Adsorption of Detergent on Cotton. An 0.01% solution of radioactive sodium dodecyl benzene sulfonate was prepared. Eight pieces of cotton cloth, approximately 1¾ in. in diameter, were immersed in separate 25-ml. portions of the solution for 30 min. at 35°C. The pieces were rinsed by dipping successively into four 600-ml. beakers, containing 400 ml. of distilled water at 35°C. The water in the beakers was changed after rinsing two pieces. The cloth was dried on a copper screen in an oven at 105°C., with the screen raised slightly from the shelf. The pieces were clamped in a circular aluminum holder so that a circle of cloth, 1⅜ in. in diameter was exposed. The radioactivity was measured in a windowless counter. Counts were made for one minute, and the average count for the eight pieces was calculated. If necessary, counts were made for longer than a minute to bring the total counts for the eight pieces to 1,000 above background.

0.01, 0.05, 0.10, and 0.15% solutions of the radioactive detergent were prepared with the following builders at concentrations of 1, 2, 4, 10, and 20 x 10^{-3} molar in $(Na)^+$ from the builder: sodium chloride, sodium sulfate, sodium carbonate, trisodium phosphate, tetrasodium pyrophosphate, and sodium tripolyphosphate. Pieces of cotton cloth were dipped in the solutions and rinsed as described above. The pH of all solutions, as prepared, was determined with a Beckman pH meter. The counts per minute for material adsorbed from corresponding solutions with no builder were arbitrarily taken as 100, as an adsorption measure. The relative adsorption on the cloth for the various builders was calculated by dividing the counts by the counts without builder and multiplying by 100. The results are shown in Table II.

About the same adsorption was obtained with detergent alone and with sodium chloride as builder. A moderate reduction was found for sodium sulfate. The significance is doubtful however, based on the statistical accuracy of counting. Tetrasodium pyrophosphate and sodium tripolyphosphate caused the greatest reduction in adsorption in all cases. Sodium carbonate and trisodium phosphate gave adsorptions between sodium sulfate and the molecularly dehydrated phosphates. With the exception of sodium chloride and sodium sulfate at a detergent concentration of 0.01-0.05%, relatively sharp reductions in the amount of detergent occurred at 1–4 x 10^{-3} molar sodium ion concentration.

Adsorption of Detergent on Soils. A synthetic soil (A), which corresponds closely, in carbon and mineral constituents, to shipboard soil (12), was formulated as follows: 7 parts pulverized silica, 1 part lampblack, 1 part ferric oxide, 1 part iron powder, and 21 parts magnetite.

50-mg. portions of the soil were placed in 250-ml. Erlenmeyer flasks, containing 25 ml. of radioactive detergent solution (0.10%) alone and detergent solutions containing the various builders at the same anion concentration of 4 x 10^{-3} molar. The flasks were shaken for one-half hour in apparatus which provided wrist-action motion. The solutions were filtered with suction on double No. 40 Whatman paper, using a stainless steel filter (13). The flasks were washed twice with 2-ml. portions of distilled water, and the paper and precipitate were washed 4 times with 5-ml. portions of distilled water. The papers and precipitates were dried overnight in a desiccator, containing phosphorus pentoxide, to reduce curling. The papers were counted in the flow counter, and relative adsorption was determined as in the case of adsorption on cotton. Runs were made on three successive days. Adsorption on cotton cloth was also determined for the same detergent and builder concentrations for comparison. The results are shown in Table III. Tests indicated that magnetite does not adsorb appreciable amounts of detergent. The reduction in adsorption for Soil (B), formulated similar to (A) except without magnetite and iron powder, is shown for the phosphate builders in Table III. The effect of pH was determined with the phosphates as builders at constant molarity in $(Na)^+$ and also constant molarity in phosphate. The results are shown in Table IV.

Quantitative determinations of the adsorption of detergent on cotton and of the various soil constitu-

TABLE IV

Effect of pH on Adsorption of Detergent [a]

Builder	Builder concentration	pH	Relative adsorption on soil A
Trisodium phosphate	8 x 10^{-3} molar $(Na)^+$	11.3	12
Tetrasodium pyrophosphate	8 x 10^{-3} molar $(Na)^+$	11.3[b]	10
Sodium tripolyphosphate	8 x 10^{-3} molar $(Na)^+$	11.3[b]	9
Trisodium phosphate	8 x 10^{-3} molar $(Na)^+$	8.8[c]	12
Tetrasodium pyrophosphate	8 x 10^{-3} molar $(Na)^+$	8.8[c]	10
Sodium tripolyphosphate	8 x 10^{-3} molar $(Na)^+$	8.8	8
Trisodium phosphate	4 x 10^{-3} molar (phosphate)	11.3	16
Tetrasodium pyrophosphate	4 x 10^{-3} molar (phosphate)	11.3[b]	9
Sodium tripolyphosphate	4 x 10^{-3} molar (phosphate)	11.3[b]	7
Trisodium phosphate	4 x 10^{-3} molar (phosphate)	9.0[c]	13
Tetrasodium pyrophosphate	4 x 10^{-3} molar (phosphate)	9.0[c]	8
Sodium tripolyphosphate	4 x 10^{-3} molar (phosphate)	9.0	9

[a] 0.1% sodium dodecyl benzene sulfonate.
[b] Adjusted with sodium hydroxide solution.
[c] Adjusted with hydrochloric acid solution.

TABLE V

Adsorption of Detergent[a] from Solutions Containing Builders

Builder,[b] cotton or soil	Millimols adsorbed (× 1,000)[c] on:					
	Cotton cloth	Carbon black	Iron oxide (Fe_3O_4)	Iron oxide (Fe_2O_3)	Pulverized silica	Iron by hydrogen reduction
None	1.43	0.80	0.57	0.14	0.06	0.06
Sodium chloride	1.55	0.60	0.20	0.09	0.03	0.06
Sodium sulfate	1.32	0.69	0.20	0.06	0.03	0.03
Sodium carbonate	1.26	0.55	0.14	0.06	0.00	0.03
Trisodium phosphate	1.23	0.40	0.03	0.06	0.00	0.03
Tetrasodium pyrophosphate	1.00	0.34	0.03	0.03	0.00	0.01
Sodium tripolyphosphate	1.00	0.37	0.03	0.03	0.00	0.01

[a] 0.1% sodium dodecyl benzene sulfonate. [b] 2×10^{-2} molar $(Na)^+$. [c] Cotton cloth was piece 1¾ in. in diameter, soil constituents were 50 mg.

ents described under Materials and Reagents were made with (radioactive) detergent concentration at 0.10% and builder concentration at 2×10^{-2} molar $(Na)^+$. Pieces of cotton cloth were immersed in the solutions and washed as previously described. They were extracted four times with boiling alcohol. The collected extracts were evaporated to a low volume and made up to 5 ml. with absolute alcohol. Portions of the solution were spread uniformly on aluminum planchets 1¾ in. in diameter, dried, and counted in the flow counter. The counts were compared with those obtained with a standard solution of detergent, and the amount of detergent adsorbed was determined by direct proportion. Counts made of the extracted cloth showed that the extraction was practically complete. The results are shown in Table V. 50-mg. portions of the various soil constituents were placed in 250-ml. Erlenmeyer flasks. The solutions were shaken and filtered, and the precipitates were washed as previously described. The papers were extracted four times with boiling alcohol, and the collected extracts were evaporated to a small volume. The amount of detergent adsorbed was determined, similar to the method used for cotton cloth. The results are shown in Table V.

Adsorption of Builders. Quantitative determinations were made of the amount of builders adsorbed on cotton and the various soil constituents excepting magnetite. Solutions of non-radioactive detergent (0.10%) were prepared with builder concentrations of 2×10^{-2} molar $(Na)^+$. The builders were radioactive except sodium chloride. The specific activities were approximately 0.07 microcuries per ml. for sodium sulfate and 0.04 microcuries per ml. for the remainder of the builders. Pieces of cotton were immersed as previously described. The pieces were extracted four times with boiling water, and the adsorption was determined by radioactivity measurements in a manner similar to that used in the case of detergents. The extracted pieces of cloth were also counted in the flow counter. Very little activity remained except in the case of trisodium phosphate, for which it was estimated that about 40% of the activity remained on the cloth. This residue was attributed to chemical adsorption. The amount of sodium chloride adsorbed was determined by measurement of sodium, using a Beckman Flame Photometer.

To measure adsorption on carbon black, 50-mg. samples were shaken with the various solutions and filtered and washed as previously described. Attempts to extract carbon residues were made but were not considered complete because of difficulty in wetting the carbon. Therefore the filter papers were dried in a desiccator over phosphorus pentoxide and counted in the flow counter. To determine the amount of builder adsorbed, standards were prepared by mixing known amounts of builders in small portions of detergent solution with 50-mg. portions of carbon black in stainless steel planchets of the same diameter as the filter paper used. The detergent was added to facilitate wetting. The pasty mixture was dried and counted. The amount of builder was determined by direct proportion. The results for cotton and carbon black, calculated as millimols of anion, are shown in Table VI. No determination for sodium chloride was made, using the flame photometer, because of high sodium blanks. Magnetite was not used in the adsorption studies of builders because it appeared to react chemically with the phosphate builders. The amount of builders adsorbed on the other soil constituents was negligible, being on the order of 10^{-4} millimols or less per 50 mg.

TABLE VI

Adsorption of Builders from Aqueous and Detergent[a] Solutions

Builder[b]	Millimols anion adsorbed (× 1,000)			
	No detergent		With detergent	
	On cotton (1⅜ in. dia. circle)	On carbon black, 50 mg.	On cotton (1⅜ in. dia. circle)	On carbon black, 50 mg.
Sodium chloride	2.90	......	2.56	......
Sodium sulfate	1.26	0.07	1.20	0.07
Sodium carbonate	1.23	0.09	1.23	0.09
Trisodium phosphate	1.40	0.43	1.40	0.55
Tetrasodium pyrophosphate	0.68	0.04	0.64	0.04
Sodium tripolyphosphate	0.52	0.03	0.54	0.03

[a] 0.10% sodium dodecyl benzene sulfonate.
[b] 2×10^{-2} molar $(Na)^+$.

Discussion

Meader and Fries (14) have presented similar studies in the adsorption of labelled sodium dodecyl benzene sulfonate on cotton in the presence of sodium sulfate and sodium pyrophosphate. These workers reported that less detergent was adsorbed in the presence of tetrasodium pyrophosphate than when sodium sulfate was used as a builder. This result is parallel to that obtained in the present study. However Meader and Fries reported that the addition of these salts increased the adsorption of detergent whereas in the present study a decrease was found for these and other builders except sodium chloride, for which no significant change was noted. The decreased adsorption was obtained over a wide range of experiments, including adsorption on soil. The effect was more pronounced in the case of soils. Sodium chloride also caused reduced adsorption in the case of soils. In the present study the conditions of adsorption and desorption represent conditions which might be found in a normal washing cycle. The adsorption values given are not true adsorption values but rather represent material retained after the described rinsing procedure. In this respect it may be noted that the procedure of Meader and Fries, which was markedly different than the present procedure, does give true adsorption data.

Sanders and Lambert (15) presented data on the improved detergency of an alkyl aryl sulfonate in the presence of tetrasodium pyrophosphate and carboxymethyl cellulose as builders. These authors showed that the addition of builders did not influence significantly the surface tension (against Nujol), the wetting time, or dye solubilization action of either an alkyl aryl sulfonate or non-ionic detergent solution. They concluded that the beneficial effect of builders is not attributable to any change in the surface activity of the detergent. It was postulated that the builder might act by a) swelling the fiber interstices, b) entering into ion exchange with soil constituents, c) influencing the degree of adsorption of surfactant by the fiber, and d) increasing the negative charge on the soil and fiber through an electrostatic effect. Various functions of builders have been listed by Niven (16). The list of functions does not explain why one builder is better than another or why one builder is better for a particular application. Referring to postulate c), the degree of adsorption was decreased with all builders except for adsorption on cotton, using sodium chloride as a builder. The adsorption decreased markedly with a small increase in builder concentration and was then constant over a comparatively wide range. There appears to be a decrease of adsorption with increase of valence of the anion, but only of a qualitative nature. There does not appear to be direct competition for sites on cotton and soils between builder and detergent because there was no significant difference in builder adsorption whether detergent was present or not. In this connection it may be noted that only 3 and 4 x 10^{-5} millimols of sodium tripolyphosphate and tetrasodium pyrophosphate are adsorbed on 50 mg. of carbon black, but the amount of decrease of detergent adsorbed is large in comparison, from 8 x 10^{-4} to 3-4 x 10^{-4} millimols with addition of the builders. The pH did not appear to be a significant factor in adsorption.

Tests conducted by the authors (17) have shown that, with the sodium concentration at 1 x 10^{-2} molar, the same amount of micelles was formed for each of the builders at a detergent concentration of 0.1%. Also with sodium chloride and sodium tripolyphosphate at 1 x 10^{-2} molar sodium $(Na)^+$ the same percentage of micelles was found for both over a detergent range of 0.05% to 0.30%. Therefore the amount of micelles present does not appear to be a significant factor in adsorption.

It may be postulated that the charge on the anion of the builder is the main effect in causing reduction in adsorption of the detergent. It may be further postulated that the effect is modified as a function of the concentration of the various solutes. Calculations were made of the activity coefficient of the anion of the detergent, designated as R, using the formula of Debye and Hückel (18, 19), in a reduced form as follows:

$$\log y_i = \frac{0.5\sqrt{\mu}}{1+\sqrt{\mu}}$$

where

y_i = activity of coefficient of ion species i

μ = ionic strength = $\frac{1}{2}\,(C_1Z_1^2+C_2Z_2^2+C_3Z_3^2)$

Z_i = valence of ion species i

C = concentration of each ion species in mols per liter

The values obtained for a detergent concentration of 0.1% (0.0028 molar) and builder concentrations of 0.001, 0.010, and 0.020 molar $(Na)^+$ are shown in Table VII.

The only variable in the calculations was the term $C_iZ_i^2$ for builders. The values for this term are shown in Table VIII.

The following considerations may be noted in the application of the formula. Very dilute solutions of strong electrolytes, such as ionic detergents and most builders, act as ideal solutions. At high concentrations, probably at the range where significant amounts of micelles form, part of the solution may be considered as molecules. The activity coefficient is a measure of the extent to which the properties of a species of ion in solution are a function of the concentration. For example, in Table VII, 0.943 (no builder) means that the activity of the anion is 0.943 of what it would be if the $(Na)^+$ of NaR had no influence whereas, with sodium tripolyphosphate present at 0.01 molar $(Na)^+$, it is reduced to only 0.838. No quantitative relation could be made between the decrease in adsorption of detergent as a function of increase of valence on the anion of the builder, but the qualitative relation between the decrease of activity coefficient of R and decrease in adsorption is good, especially for molarity of 0.001 and 0.01 $(Na)^+$ concentrations. If the reduction in adsorption were related directly to the activity coefficient, it would be expected that less adsorption of detergent would occur at 0.02 molar $(Na)^+$ concentration of builder than at 0.01 molar. However about the same reduction in adsorption was found for both concentrations.

TABLE VII

Activity Coefficient of Anion of Sodium Dodecyl Benzene Sulfonate

Molarity of builder in sodium $(Na)^+$	0.001	0.010	0.020
Builder:			
None	0.943	0.943	0.943
Sodium chloride	0.935	0.890	0.860
Sodium sulfate	0.932	0.874	0.838
Sodium carbonate	0.932	0.874	0.838
Trisodium phosphate	0.928	0.860	0.821
Tetrasodium pyrophosphate	0.925	0.848	0.807
Sodium tripolyphosphate	0.922	0.838	0.794

TABLE VIII

$\Sigma\, C_iZ_i^2$ for Builders

Molarity of builders $(Na)^+$	0.001	0.010	0.020
Builder:			
Sodium chloride	0.002	0.02	0.04
Sodium sulfate	0.003	0.03	0.06
Sodium carbonate	0.003	0.03	0.06
Trisodium phosphate	0.004	0.04	0.08
Tetrasodium pyrophosphate	0.005	0.05	0.10
Trisodium pyrophosphate	0.006	0.06	0.12

Theoretical calculations by Osipow and Snell (20) indicate that builder anions contribute to the effective charge on surfaces of soil and fabric and support the assumption that anions, other than those directly adsorbed on the surface of particles, contribute to the effective charge. The calculations also indicate that the surface-charge density increases with the valence of the anion.

From the adsorption data no suitable theories could be postulated as to why one builder acts better than another. The beneficial effect of builders may be chiefly due to the nature of builder-detergent solution effects, *e.g.*, ability to prevent redeposition of soil. In this connection it is known that, at moderate concentrations, polyphosphates do not promote the deposition of soil onto cotton but that more alkaline builders do promote soil deposition.

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The Phosphorus Content of Refined Soybean Oil as a Criterion of Quality

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DURING THE PAST TWO DECADES or more, ways for improving the flavor stability of soybean oil used for edible purposes have received much attention. However present procedures for refining crude soybean oil generally place major emphasis on the attainment of a minimum loss of oil and on a specified color for the finished product. The refiner varies the quantity and concentration of alkali solution used in the neutralization step in accordance with the characteristics of each lot of oil and thus determines to a large extent the resultant color reduction and oil loss. Although flavor stability of the refined oil is influenced by conditions employed in the neutralization step, a search of the literature revealed little information on this aspect. The Soybean Oil Committee of the Soybean Research Council for the National Soybean Processors' Association published a number of factors that affect flavor stability (9). One of the factors listed as favorable was the use of a slight excess of caustic. Mattikow stated that the phosphorus content of a refined oil should not exceed 0.5 part per million (6). Neither Mattikow nor the Soybean Oil Committee gave any data to support their conclusions. Sanders found a correlation over a restricted range between bleached color and stability where reduction in color favored stability (8).

Because of the lack of specific information on the subject, a study on a pilot-plant scale was undertaken to investigate the relationship between conditions employed in refining a crude oil and the stability of the finished oil. Both degummed and non-degummed crude oils were used in the tests. The data obtained in this study and the conclusions reached are presented here.

Small individual batches of oil taken from a large blended batch were refined with lyes ranging from 8° to 30° Baumé and with several amounts of sodium hydroxide varying from 0.05 to 0.30% in excess of the amount required to neutralize the free fatty acids, based on weight of the oil. Samples of the refined, bleached, and deodorized soybean oil produced by the refining treatments were analyzed for iron, tocopherol, phosphorus, and ash. The effect of refining conditions on the removal of these substances, and on the color and stability of the deodorized oil as measured by the Active Oxygen Method could then be determined. All of the oils were refined by the batch method.

Experimental Methods

Each refining test was conducted with 120 lbs. of oil. The oil was agitated vigorously at room temperature in a kettle while the alkali solution was slowly added, and mixing was continued for 15 min. After the speed of the agitator had been reduced to a low rate, the material was heated to 150°F.(65°C.) and pumped to a centrifuge. About 25 min. were required to complete the separation of the oil and soapstock. The refined oil was next washed with 15% of softened water, heated to 205° to 210°F.(95° to 98°C.), and centrifuged. The warm oil was dried by slowly drawing it back into the kettle under a vacuum of 28 to 29.5 in. of mercury, heating it to 210° to 215°F.(98° to 102° C.), and filtering it.

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