action may have a significant effect on relative ratings.

With the soiling conditions employed in the tests, it has been determined that the initial soil level on a swatch may vary over a considerable range without affecting significantly soil removal values. Estimates of precision and reproducibility of soil removal and whiteness retention determinations indicate that they are adequate in terms of differences being measured.

Soil removal evaluations have been made with a number of different types of detergents using dry carbon soil, and a carbon-mineral oil combination. The two soils were found to give the same relative ratings of the detergents.

Using a series of 12 detergents representing different types, soil removal and whiteness retention values determined with the tracer methods have been compared with values obtained with conventional laboratory test methods. Soil removal evaluations differ considerably with the two methods, and noncorrelating results can be related to the general types of detergent compositions involved. The tracer method appears to give evaluations free of some anomalies that have been recognized in the conventional laboratory tests.

It is believed that the use of radioactive soils in laboratory evaluations will permit studies with soil types approaching natural soils more closely than have the soils used in conventional methods. Use of tracer methods in conjunction with conventional tests should provide for more reliable laboratory evaluations of detergency.

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Synthetic Detergents from Animal Fats. IV.[1] Sodium 9,10-Dichlorooctadecyl Sulfates[2]

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SULFATED hydrogenated tallow alcohols (sodium tetradecyl, hexadecyl, and octadecyl sulfates) are good detergents and surface-active agents, with some disadvantage because of limited solubility in water at room temperature. Sulfated tallow alcohols (mainly sodium tetradecyl, hexadecyl, octadecyl, and oleyl sulfates) are likewise good detergents and surface-active agents, adequately soluble because of the presence of sodium oleyl sulfate. Retention of unsaturation appears desirable but may be difficult, depending upon the reduction and sulfation methods selected (7).

Acting upon a suggestion of John C. Cowan, Northern Utilization Research Branch, we have found that chlorinated tallow alcohol sulfates (sodium tetradecyl, hexadecyl, octadecyl, and 9,10-dichlorooctadecyl sulfates) can be prepared by the addition of chlorine to the unsaturated constituents of tallow alcohols (mainly oleyl alcohol) and sulfation of the chlorinated tallow alcohols with chlorosulfonic acid. This method has the advantage that it does not require the use of a special sulfating agent to avoid reactions involving the double bond; and the sulfated chlorinated tallow alcohols are adequately soluble at room temperature.

The present paper is concerned with preparation of sodium 9,10-dichlorooctadecyl sulfates from oleyl and elaidyl alcohols, and the chlorination and sulfation of tallow alcohol. The products have been compared and evaluated in terms of solubility, surface and interfacial tension, calcium stability, wetting properties, stability to hydrolysis, foam height, and detergency.

Sodium 9,10-Dichlorooctadecyl Sulfates

9-Octadecenols. Oleyl alcohol (I no. 92.5, theoretical value 94.5) and elaidyl alcohol (I no. 94.7, m.p. 36.1-37.0°) were prepared from a commercial oleyl alcohol as described in previous publications (5, 7).

9,10-Dichlorooctadecanols. Chlorination was carried out according to a method for the chlorination of unsaturated alcohols described to us by H. M. Teeter (6), Northern Utilization Research Branch, modified by use of a lower reaction temperature and lower solvent ratio.

A slow stream of chlorine was introduced into a stirred solution of 100 g. of purified oleyl alcohol in 300 ml. of dichloromethane, cooled in a dry ice-carbon tetrachloride bath maintained at —45°. Chlorine was passed in at such a rate that the reaction temperature remained in the range —13° to —23° throughout 4.5 hours. Completion of reaction was indicated by the development of a yellow-green color in the solution and a fall in reaction temperature as a result of no further heat of reaction. Solvent and excess chlorine were removed at reduced pressure in a stream of nitrogen, finally being heated on the steam bath to remove the last trace of solvent. 9,10-Dichlorooctadecanol was obtained as a colorless oil, yield 97%, m.p. 12°, n_D^{20} 1.4760, d_4^{20} 0.9898, molecular refractivity 96.71 (theoretical value 96.58), I no. 0.3, 19.95% Cl (calculated for $C_{18}H_{36}Cl_2O$, 20.90% Cl; calculated with correction for saturated impurities in the oleyl alcohol, 20.45% Cl).

Elaidyl alcohol chlorinated in the same manner gave a different racemic mixture, a 9,10-dichlorooctadecanol, a white solid, m.p. 31°, yield 94%, n_D^{20} 1.4757, d_4^{20} 0.9946, molecular refractivity 96.19, I no. 0.3, 20.59% Cl.

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[1] I, II, and III in this series are references (5), (4), and (7), respectively.

[2] Presented at the meeting of the American Oil Chemists' Society in Minneapolis, October 1954.

[3] A laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

Sulfation of 9,10-Dichlorooctadecanols. Chlorosulfonic acid, 0.15 mole, was added dropwise to a cold, stirred solution of 0.12 mole of the 9,10-dichlorooctadecanol (from oleyl alcohol) in 100 ml. of chloroform at 6° to 10°. The reaction mixture was heated to 37°, maintained 0.5 hour at 37°, and cooled. n-Butanol, 100 ml., was added, the mixture was neutralized with 18 N sodium hydroxide, and water and chloroform were removed together by distillation. The dry, boiling butanol solution was filtered to remove inorganic salts, then cooled to —25°, and filtered to give a 65% yield of a sodium 9,10-dichlorooctadecyl sulfate as a light cream colored solid. Purification by carbon treatment and recrystallization from butanol at —25° gave a 39% yield of a sodium 9,10-dichlorooctadecyl sulfate, a white solid, I no. 0.1, containing 5.01% Na, 7.07% S, and 15.39% Cl (calculated for $C_{18}H_{35}Cl_2NaO_4S$, 5.21% Na, 7.26% S, 16.06% Cl; 15.72% Cl when corrected for saturated impurities present in the oleyl alcohol).

Sulfation of the 9,10-dichlorooctadecanol from elaidyl alcohol gave 84% yield of a light cream-colored solid. Purification gave 67% yield of a sodium 9,10-dichlorooctadecyl sulfate, a white solid, I no. 0.7, containing 5.27% Na, 7.14% S, and 15.87% Cl.

Sulfated Chlorinated Tallow Alcohol

A tallow alcohol,[4] acid no. 1.5, saponification no. 8.2, I no. 54.1, % hydroxyl 6.4, was chlorinated and sulfated as described for oleyl alcohol except that chloroform was used as the solvent, the chlorinated tallow alcohol was not isolated, and purification steps were omitted.

Chlorine was run slowly into a solution of the tallow alcohol in 3 volumes of chloroform at —20° until an excess of chlorine was evident. Excess chlorine was expelled by a stream of nitrogen. The iodine absorption of the solution at this point was 0.13 g. per 100 ml., indicating almost complete reaction of chlorine with unsaturated constituents.

Without removal of solvent, the chlorinated tallow alcohol was sulfated with 1.09 molar ratio of chlorosulfonic acid at 0° to 10°. Methanol was added, and the cold reaction mixture was neutralized with 18 N sodium hydroxide and evaporated to dryness to give a cream-colored solid. Separation behavior of a sample, between butanol and water, indicated that the product contained about 90% active ingredient.

Solubility

The sodium 9,10-dichlorooctadecyl sulfates from either oleyl or elaidyl alcohol are readily soluble, but the solubility is difficult to measure. Like sodium oleyl sulfate, a 20% solution forms a clear gel at room temperature. From qualitative observations it appears that sodium 9,10-dichlorooctadecyl sulfates, like sodium oleyl sulfate or sodium elaidyl sulfate, are able to solubilize, to some extent, the difficultly soluble sodium hexadecyl sulfate and sodium octadecyl sulfate. The solubility of a mixture of pure compounds representing sulfated chlorinated tallow alcohol is about 0.2% at 25°. The solubility of a mixture representing sulfated hydrogenated tallow alcohol is about 0.02%.

Surface and Interfacial Tension

Figure 1 shows the surface tension *vs.* concentration curves for the sodium 9,10-dichlorooctadecyl sulfates from oleyl and elaidyl alcohol. Surface tension was measured at 25° with the Du Noüy tensiometer. Values for surface and interfacial tension are also given in Table I.

The curves differ only in the range near the critical micelle concentration. The sodium 9,10-dichlorooctadecyl sulfate from oleyl alcohol is not quite so pure, and the minimum is more pronounced. Interfacial tension values at 0.1% concentration, against a refined mineral oil, for the two compounds are slightly less than the value for sodium oleyl sulfate and considerably less than the value for sodium dodecyl sulfate (Table I).

Calcium Stability

The calcium stability of the sodium 9,10-dichlorooctadecyl sulfates, measured by a modified Hart method (8), is recorded in Table I. The values are intermediate between those for sodium dodecyl sulfate and sodium oleyl sulfate.

Wetting Properties and Stability to Hydrolysis

Wetting properties of the sodium 9,10-dichlorooctadecyl sulfates, measured with a standard binding tape (3), are recorded in Table I. The compounds are somewhat less effective wetting agents than sodium dodecyl sulfate or sodium oleyl sulfate. Under the conditions of the test described in Table I, 0.1% solutions of the sodium 9,10-dichlorooctadecyl sulfates, in 1% sodium hydroxide have about the same wetting properties before and after boiling for 4 hours. Like sodium dodecyl sulfate or sodium oleyl sulfate, they appear to be resistant to alkaline hydrolysis, at least at the sulfate linkage. The sinking time measurements show that the four compounds, as might be expected, are hydrolyzed in hot 5% sulfuric acid solutions.

Foam Height

Foaming properties, measured by the Ross-Miles test (2), are recorded in Table II as the foam height 5 min. after formation. Mixtures A, B, and C are mixtures of pure compounds, representing the com-

TABLE I

Surface and Interfacial Tension, Calcium Stability, and Wetting Properties

	Surface and interfacial tension, 0.1% solutions, 25° dynes/cm.		Ca stability, p.p.m. $CaCO_3$ (8)	Sinking time (3), 0.1% concentration of surface-active agent, 25°, seconds				
	S.T.	I.T.		Distilled water	1% NaOH	Boiled 4 hours in 1% NaOH	5% H_2SO_4	Boiled 0.5 hours in 5% H_2SO_4
Na dodecyl sulfate	49.0	20.3	550	13	13	17	15	>600
Na oleyl sulfate	35.0	7.4	$>1,800$	19	23	31	30	>600
Na 9,10-dichlorooctadecyl sulfate (from oleyl alcohol)	35.8	5.8	970	32	53	46	62	>600
Na 9,10-dichlorooctadecyl sulfate (from elaidyl alcohol)	35.8	6.0	950	39	66	57	70	>600

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[4] Prepared by Ethyl Corporation.

position of sulfated tallow alcohol, sulfated hydrogenated tallow alcohol, and sulfated chlorinated tallow alcohol, respectively. The mixtures are based on the fatty acid composition of tallow as being, for this purpose, approximately 6% myristic, 28% palmitic, 16% stearic, and 50% oleic acid. Thus A contained 6% sodium tetradecyl sulfate, 28% hexadecyl, 16% octadecyl, and 50% sodium oleyl sulfate; B contained 6% tetradecyl, 28% hexadecyl, and 66% sodium octadecyl sulfate; C contained 6% tetradecyl, 26% hexadecyl, 14% octadecyl, and 54% sodium 9,10-dichlorooctadecyl sulfate (from oleyl alcohol).

TABLE II

Foam Height and Detergency

	Foam height[1] (2), 60°, mm.		Detergency,[2] 60° △ R values	
	0.25% in distilled water	0.1% in hard water of 100 p.p.m.	0.1% in hard water of 100 p.p.m.	0.25% in hard water of 300 p.p.m.
Sodium dodecyl sulfate	175	248	24.8	24.5
Sodium oleyl sulfate	240	226	34.8	24.0
Sodium 9,10-dichlorooctadecyl sulfate (from oleyl alcohol)	235	205	31.5	22.2
Sodium 9,10-dichlorooctadecyl sulfate (from elaidyl alcohol)	245	209	32.8	21.7
Sulfated chlorinated tallow alcohol (90% active ingredient)	238	208	29.5	22.9
Mixture A[3] (Representing sulfated tallow alcohol)	249	216	30.7	26.1
Mixture B[3] (Representing sulfated hydrogenated tallow alcohol)	244	72	36.8	34.4
Mixture C[3] (Representing sulfated chlorinated tallow alcohol)	243	206	34.8	24.5

[1] Measured 5 min. after formation.

[2] Terg-O-Tometer, G.D.C. No. 26 standard soiled cotton, 10 swatches/l., 20 min. at 60°, 110 cycles/min.

[3] A, B, C are mixtures of pure compounds representing the composition of sulfated tallow alcohol, sulfated hydrogenated tallow alcohol, and sulfated chlorinated tallow alcohol, respectively.

Sodium dodecyl sulfate had poor foam stability in distilled water. The mixture representing sulfated hydrogenated tallow alcohol had the least foam in hard water. There was comparatively little difference in foaming properties of sodium oleyl sulfate, sodium 9,10-dichlorooctadecyl sulfates, sulfated chlorinated tallow alcohol (90% active ingredient), and mixtures A and C.

Detergency

Detergency was measured in the Terg-O-Tometer with G.D.C. No. 26 (1) standard soiled cotton having an initial reflectance relative to MgO as 100, 25.3; ten 2½-in. x 3¼-in. swatches per liter of solution were washed for 20 minutes at 60°, at 110 cycles per minute. Detergency was expressed as increase in reflectance, △ R, after washing (Table II).

In the tests of 0.1% solutions in 100 p.p.m., a difference in △ R of 2.0 was significant with 95% probability. Under these conditions mixture B was the best detergent; mixture C was equal to sodium oleyl sulfate and somewhat better than the sodium 9,10-dichlorooctadecyl sulfates. Sodium dodecyl sulfate was the least effective detergent.

In the tests of 0.25% solutions in 300 p.p.m., a difference in △ R of 1.6 was significant with 95% probability. Under these conditions mixture B was again the best detergent, mixture A was better than C, which was equal to sodium dodecyl sulfate and sodium oleyl sulfate. The detergency of the sodium 9,10-dichlorooctadecyl sulfates was unfavorably affected when water hardness was increased from 100 to 300 p.p.m.

The sodium 9,10-dichlorooctadecyl sulfates resemble sodium oleyl sulfate in detergency characteristics. Mixture C was better than A at 0.1% in 100 p.p.m. and slightly inferior to A at 0.25% in 300 p.p.m.

With a different standard soiled cloth, A.C.H. No. 114,[5] tests of 0.1% solutions in hard water of 100 p.p.m. showed that the sodium 9,10-dichlorooctadecyl sulfates were better than sodium dodecyl sulfate but somewhat inferior to sodium oleyl sulfate in detergency.

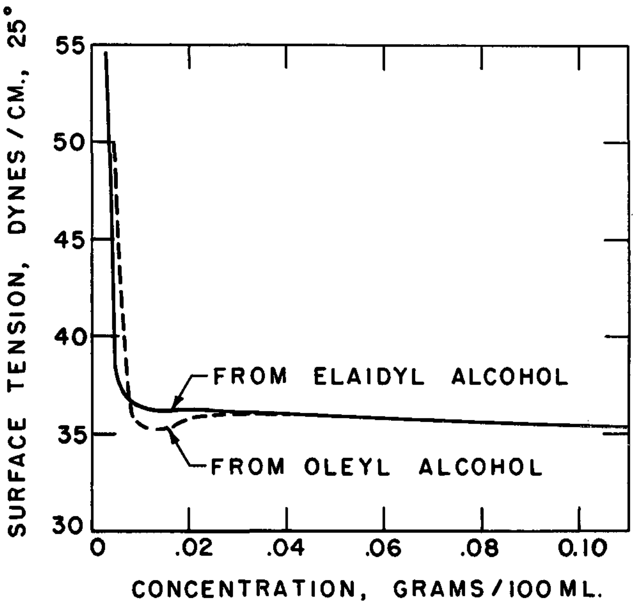

FIG. 1. Surface tension of sodium 9,10-dichlorooctadecyl sulfates.

Summary

Sodium 9,10-dichlorooctadecyl sulfates were prepared by the addition of chlorine to oleyl and to elaidyl alcohols, and sulfation of the dichlorooctadecanols with chlorosulfonic acid. The sodium 9,10-dichlorooctadecyl sulfates are readily soluble in water at 25° and resemble sodium oleyl sulfate in detergent and surface-active properties. Tallow alcohols can be chlorinated by the addition of chlorine and sulfated with one of the usual sulfating agents to produce an adequately soluble detergent and surface-active agent.

Acknowledgment

We are pleased to acknowledge the suggestion of John C. Cowan from which this work originated, and the assistance given to us by H. M. Teeter and E. W. Bell, all of the Northern Utilization Research Branch in furnishing us with an initial quantity of 9,10-dichlorooctadecanol (from oleyl alcohol), and a procedure for the chlorination of oleyl and elaidyl alcohols.

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[5] American Conditioning House Inc. Mention of a particular test cloth does not constitute recommendation by the Department of Agriculture over similar products not mentioned.

Microanalyses for chlorine and sulfur were performed by Mrs. Ruth B. Kelly.

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The Reduction of Free Gossypol in Cottonseed Flakes During Solvent Extraction

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As is common to most vegetable oil seeds, cottonseed contains small amounts of pigments such as carotenoids and chlorophyll. However, from the standpoint of oil extraction, the most important cottonseed pigment is a yellow solid called gossypol, which is unique to cottonseed. Because of its toxic properties the removal or destruction of gossypol in processing cottonseed meal is important. The pigments are located throughout the tissue of the meats in glands, which are strong, semi-rigid, ovoid-shaped cells about 100 microns long (3). If the gland wall holding the gossypol can be ruptured, the gossypol is converted to a non-toxic form, called "bound" gossypol. In contrast, the "unbound" or toxic gossypol is called "free" gossypol. Because of their small size the cells are generally not ruptured in the various mechanical operations carried out on the seed during the oil removal. Heating, in the presence of moisture, will effectively rupture the pigment glands, but the degree of heating required to accomplish this also denatures the proteins (12, 13), reducing their nutritional value (10). This denaturing is indicated by a reduced solubility in both 3% sodium chloride solutions and water. The solubilities of the gland walls in various dehydrated solvents has been studied by Dechary and co-workers (6), who report that the alcohols and ketones are the most effective solvents. Olcott (9) reports that gossypol is almost completely extracted by chlorinated hydrocarbon solvents, but Boatner (2) found that pigment glands in sliced sections of cottonseeds were unaffected by exposure to moisture-free trichloroethylene for 24 hrs. Commercial solvent extraction with hexane removes the gossypol to some extent, but the amount removed is variable. Wetting the flaked cottonseed with water causes immediate rupture of the pigment glands (4).

Experimental

Preliminary, small-scale experiments in this laboratory in glassware indicated that extraction of cottonseed flakes with extraction grade trichloroethylene would greatly reduce the free gossypol content of the flakes. The resulting meal could then be desolventized at a fairly low temperature with minimum damage to the proteins. In order to check these preliminary experiments cottonseed meats were next extracted in the continuous countercurrent pilot-plant extractor described by Arnold and P'Pool (1). The analysis of the cottonseed products for free gossypol was carried out according to the method of Pons and Guthrie (11). The methods used for moistures and oil were those recommended by the National Cottonseed Products Association Inc. (8). The determination of the water-soluble protein was by a modification of the method employed by Burnet and Arnold (5), using semimicro digestion followed by distillation in a Pregl apparatus.

Results

The effect of extraction temperature in reducing the free gossypol and the protein solubility of the cottonseed oil meal is shown in Figure 1. Extraction temperatures up to 122°F., while effecting a considerable reduction in gossypol content, produced only a small reduction in the water-soluble content of the extracted meal.

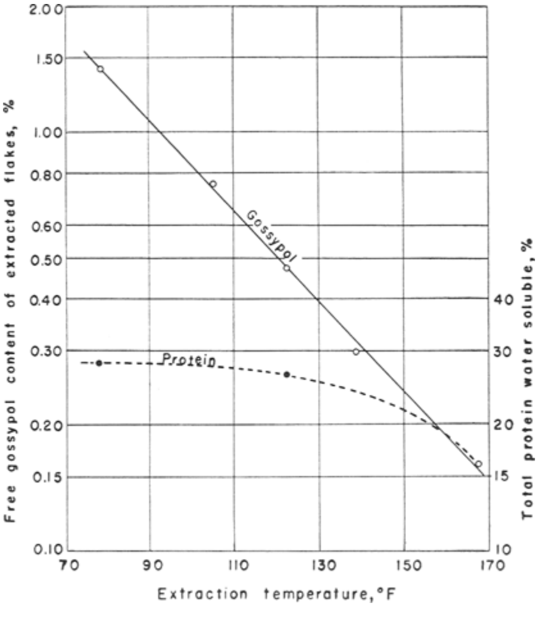

FIG. 1. Reduction of free gossypol and water-soluble protein with increase in temperature.

The most commonly used commercial method of reducing the free gossypol content of the flakes is to

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[1] Present address: Lion Oil Company, El Dorado, Ark.