ings of Cocker *et al.* (3) that the $\Delta^{\alpha,\beta}$-butenolides are more stable than the $\Delta^{\beta,\gamma}$-butenolides. The γ-lactone of 4-hydroxy-2-octadecenoic acid was isolated in relatively pure form, but the γ-lactone of 4-hydroxy-3-octadecenoic acid was merely concentrated.

Summary

Vinyl 12-ketostearate and vinyl 4-ketostearate were prepared by vinylating 12-ketostearic and 4-ketostearic acids, respectively, with vinyl acetate in the presence of a mercuric sulfate catalyst. The crude vinyl esters were purified by extracting the free fatty acids with dilute potassium carbonate, removing the mercury by distillation, and crystallizing successively from acetone and petroleum ether.

Infrared analyses revealed that lactonization occurred with the 4-ketostearic acid during the hydrogenation of the oiticica oil and during the vinylation of the keto acid. Two γ-lactones were produced. The γ-lactone of 4-hydroxy-2-octadecenoic acid was isolated in relatively pure form, and evidence was obtained for the concurrent formation of the less stable γ-lactone of 4-hydroxy-3-octadecenoic acid. The infrared spectra of the methyl keto esters, keto acids, vinyl keto esters, and the γ-lactone of 4-hydroxy-2-octadecenoic acid were determined in carbon tetrachloride solutions. It was found that the characteristic absorbances for the lactone-carbonyl, ester-carbonyl, ketone-carbonyl, and the vinyl group at about 5.6, 5.7, 5.8, and 6.1 microns, respectively, obey the Lambert-Beer law over a wide range of concentrations.

TABLE I

Absorption Bands in the Infrared Spectra of 4- and 12-Ketostearic Acids and Some of Their Derivatives

Functional group	Wavelength position of maxima (microns)[a]						
	A	B	C	D	E	F	G
C—H stretching	3.45	3.44	3.44	3.43	3.44	3.43	3.43
C—H stretching	3.52	3.51	3.53	3.51	3.52	3.51	3.51
C=O stretching ($\Delta^{\alpha,\beta}$-butenolide)	......	......	......	......	......	......	5.60
C=O stretching (acid)	......	......	......	......	5.70 5.84	5.70 5.85	......
C=O stretching (ester)	5.75	5.75	5.70	5.69	......	......	......
C=O stretching (ketone)	5.82	5.83	5.82	5.82	......	......	......
CH_2=CH stretching	......	......	6.08	6.07	......	......	......
C—H deformation	6.85	6.85	6.84	6.84	6.85	6.85	6.85
C—H deformation ($COOCH_3$)	6.97	6.97	......	......	......	......	......
C—H deformation	7.10	7.10	7.11	7.09	7.08	7.07	7.04
C—H deformation	7.37	7.35	7.37	7.34	7.32	7.31	7.42
C—O stretching	8.35 8.54	8.37 8.58	8.66	8.75	7.80	7.81	7.83 8.53
C—O—C stretching	9.16	9.04	9.17	9.04	......	......	8.89
Unassigned	9.84	9.80	......	......	......	......	9.81
CH_2=CH deformation	......	......	10.56 11.49	10.54 11.49	......	......	......
O—H deformation (COOH)	......	......	......	......	10.74	10.74	......
Lactone ring	......	......	......	......	......	......	10.99

[a] A, methyl 4-ketostearate; B, methyl 12-ketostearate; C, vinyl 4-ketostearate; D, vinyl 12-ketostearate; E, 4-ketostearic acid; F, 12-ketostearic acid; G, γ-lactone of 4-hydroxy-2-octadecenoic acid.

Acknowledgments

The authors express their appreciation to Lawrence E. Brown and Alva F. Cucullu for the elemental analyses and to Novis Smith and Edwin R. Cousins for hydrogenation of some of the oiticica oil. We are also grateful to W. G. Bickford for his many helpful suggestions. Generous samples of methyl 12-hydroxystearate were kindly supplied by The Baker Castor Oil Company, and generous samples of Brazilian oiticica oil were kindly supplied by Brazilian Industrial Oils Inc.

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[Received September 14, 1959]

The Fatty Acid Composition of Clothes Soil

W. C. POWE and W. L. MARPLE, Whirlpool Corporation, Research Laboratories, St. Joseph, Michigan

CLOTHES SOIL is a complex mixture of inorganic and organic materials. The nature of soil on clothes varies with the occupation and environment of the wearer. To attempt an analysis of all the components that occur as soil on clothing would be an impractical, if not impossible, task. The analysis can be simplified however if only the problem soils are considered. These are materials that are not removed by normal laundering procedures. Accumulated soil causes the yellowish-grey cast associated with the gradual deterioration in appearance of white garments (Figure 1). Previous work in our laboratories has shown that a major inorganic component of soil retained on clothing are clay particles that average about 0.1 μ in diameter (7). Concurrently there is an accumulation of organic material on the surface of the cotton fibers (Figure 2).

Information on the composition of this organic material is limited. Brown (1) and Oldenroth (5) extracted and analyzed freshly-adsorbed organic material from soiled garments. Brown (1) reported about 60% of the extracted soil to be free and combined fatty acids. In addition to fatty acids, he found about 15% cholesterol and fatty alcohols and 21% hydrocarbons. Oldenroth (5) reported 60–70% saponifiable material and about 8% cholesterol.

Yellowing of garments in areas that are in contact with the skin has been reported (5, 8, 10). These

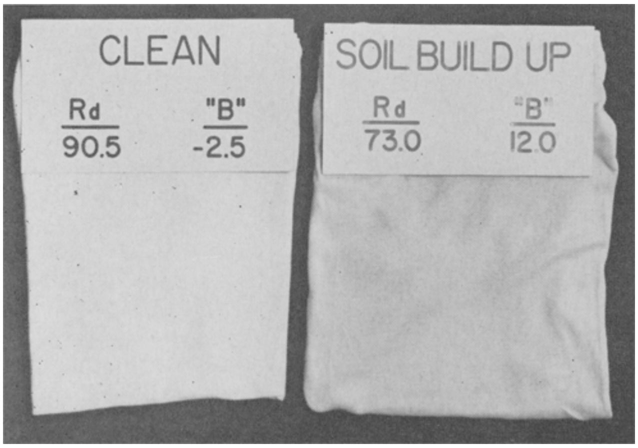

FIG. 1. Comparison of 2 T-shirts made with a Gardner Color Difference Meter. "Rd" is reflectance. The high "B" value of the soiled shirt indicates extensive yellowing.

yellow areas are not removed by normal cleaning procedures and are caused by fatty materials. Because of the large amount of saponifiable material in clothes soil and the presence of fats in yellowed areas on clothing, we analyzed for free and combined fatty acids as a first step in characterizing the organic material present as built-up soil on clothes.

Experimental

White garments that had become dingy and yellow because of accumulated soil were used for this study. These garments were laundered, to remove all the organic material possible by normal procedures, before they were extracted. The garments were extracted with a 50/50 (v/v) mixture of ethanol and trichlorethylene or with ethanol only, using a large glass Soxhlet apparatus. The solvent was removed by distillation, and the residue was dried to a constant weight at 75°C. Before analysis, particulate material was removed by filtration or centrifugation.

The insoluble fatty acid soaps were separated by Soxhlet extraction with petroleum ether. Free fatty acids were recovered by washing the petroleum ether-soluble fraction with 50% ethanol that contained 0.06N NaOH. The aqueous layer was acidified with 6N H_2SO_4, and the fatty acids were recovered in petroleum ether (4). The remaining petroleum ether-soluble material was saponified with 10% KOH in 95% ethanol (4). The reaction mixture was refluxed 2 hr. under a nitrogen atmosphere. The unsaponified fraction was collected in petroleum ether, and the fatty acids were recovered as previously described.

For gas chromatographic analysis the fatty acids were converted to methyl esters by refluxing 2 hr. under nitrogen in absolute methanol containing 1% H_2SO_4. The methyl esters were chromatographed on a 5-ft. column of 25% Reoplex 400 on Celite 545 (6). Peaks were identified by comparison with knowns, separation factors, and elimination of peaks after bromination in the case of unsaturated acids (2). Composition of the samples was calculated from planimeter measurements of peak areas.

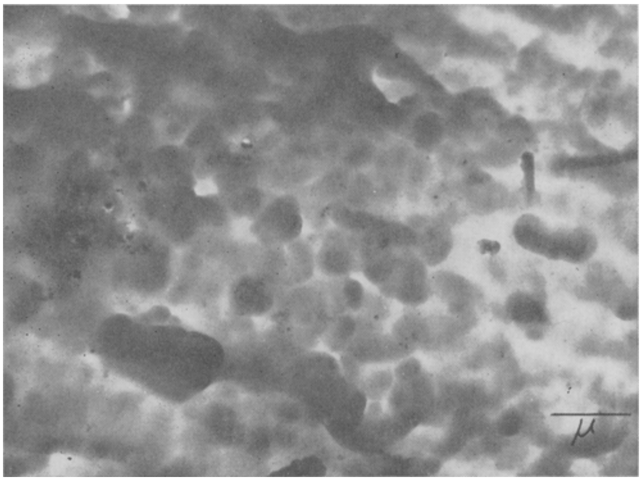

FIG. 2. Electron micrograph of accumulated soil on a cotton fiber. The fiber surface and clay particles on the fiber are covered with amorphous organic material.

TABLE I
Accumulated Organic Soil

Sample	Garment	g.	%[a]	Free fatty acids	Esterified fatty acids[b]	Lime soaps	Unsap.
A	Sheet	15.1	2.2	3.2	49.8	23.4	23.4
B	**Sheet**	31.7	4.4	2.9	58.2	20.1	18.7
C	Pooled sample[c]	15.4	......	......	......	12.5	......
D	T-shirt	8.4	7.6	......	......	38.0	......

[a] Based on wt. of garment.
[b] By difference.
[c] 4 T-shirts, 1 pillow case, 4 dress shirts.

Table I is the amount of organic material removed from various garments and a partial analysis of that material. Garment D is an extreme case of built-up soil, and sheets A and B are more representative values. The amount of free fatty acid present was very small. Insoluble fatty acid soaps were present on all the garments in significant quantities. The esterified fraction was the largest.

These data indicate that most of the organic material building up on cotton fabrics is combined fatty acids in the form of lime soaps or esters such as triglycerides. The most likely source of this fatty material is sebaceous secretions from the skin and scalp. This is particularly true for bed linens and underwear. MacKenna *et al.* (3) reported that sebum from the forearm contains 29% free fatty acids, 36% combined fatty acids, and 32% unsaponifiable material. These free fatty acids are available for heavy metal soap formation when the clothes are washed in water containing calcium or magnesium ions. Walter (10) has commented on the build-up of calcium, magnesium, and iron soaps on fabrics from free fatty acids.

The fatty acids present in built-up clothes soil are shown in Table II. These compose a series with even and odd-number carbon atoms, starting at about C_{12} and extending to C_{19} or longer. Weitkamp *et al.* have reported C_{22} acids in hair fat (11). The chain lengths C_{15}, C_{16}, and C_{18} predominate. Palmitic acid and its unsaturated homologue are present in the largest amounts. The combined C_{16} and C_{18} acids account for 70% of the total acids. About 33% of the fatty acid is palmitic acid. No linoleic or linolenic acid was detected although each is present in sebum (11).

The most unexpected result is the uniform composition of the samples. These garments came from a number of different homes and several geographical locations. The three samples extracted with ethanol-trichlorethylene are almost identical in total composition. The fatty acid composition of the free, esterified, and lime soap fractions are similar. The free fraction

TABLE II
Fatty Acids in Unremoved Clothes Soil

Carbon atoms	Percentage						
	A			B	C		D[a]
	Total[b]	Free	Lime soap	Total[b]	Total[b]	Free	Total
$<C_{12}$	1	2	....	1	1	1	6
C_{12}	1	6	....	2	2	6	1
C_{13}	2	3	....	1	1	2	....
C_{14} Myristic	6	24	6	7	9	24	7
C_{14} Unsat.	1	1	....	1	1	1	5
C_{15} Total	11	12	5	10	9	13	10
C_{16} Palmitic	33	30	38	36	33	29	30
C_{16} Branched	2	....	....	2	1	....	....
C_{16} Unsat.	10	7	16	9	11	10	9
C_{17} Total	5	2	3	6	5	4	5
C_{18} Stearic	18	6	26	18	15	5	9
C_{18} Oleic	6	7	6	5	10	5	10
$>C_{18}$	2	....	1	2	3	....	....

[a] Extracted with ethanol.
[b] Excluding lime soaps.

contains more myristic acid and less stearic acid. According to Rothman (9), there is little difference in the relative distribution of single members in free and esterified skin fat. The presence of large amounts of odd-numbered fatty acids indicates their human source. Odd-numbered normal acids have not been observed in large quantities in other materials besides human sebum (9).

The free fatty acid composition is similar to that reported by Weitkamp *et al.* (11) for hair fat and James and Wheately (2) for sebum except that the organic soil recovered from clothes has a greater amount of myristic, pentadecanoic, and palmitic acids. The amount of oleic is much less than that present in skin and hair fat. This agrees with the observation of Walter (10) that less unsaturated fatty acids are present in built-up clothes soil than in freshly-adsorbed soil. The low amount of oleic and the absence of linoleic and linolenic acids probably result from the oxidation of these compounds to polymers and other oxidation products.

Summary

Organic soil that had gradually accumulated on cotton garments and was unremovable by normal washing procedures was analyzed for free and combined fatty acids by gas-liquid chromatography.

The fatty acid composition of this material was similar to sebum and hair fat and was remarkably uniform although from several different sources and geographical locations. The predominant fatty acids were C_{15}, C_{16}, and C_{18} straight-chain acids. More than 30% of the total fatty acid was palmitic acid. The amount of oleic acid was considerably less than is reported for hair and skin fat. No linoleic acid or linolenic acid was detected. The small amount of unsaturated acids is probably the result of their oxidation to polymers and other oxidation products. The amount of free fatty acids was very small because they were converted to insoluble heavy metal soaps. Most of the combined fatty acids were present as esters, *i.e.*, triglycerides.

Acknowledgments

The authors are pleased to acknowledge the assistance of Albert Vatter, who made the electron micrograph, and of Richard A. Plunkett, of Schuman Chemical Laboratory Inc., Battle Ground, Ind., who performed the gas chromatographic analysis.

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[Received September 28, 1959]

Analysis of Surfactant Mixtures

LLOYD E. WEEKS and JOHN T. LEWIS, Monsanto Chemical Company, St. Louis, Missouri

ALTHOUGH MANY METHODS have been presented for analysis of surface-active agents, none have actually been based on analysis of built detergent compositions containing surfactants which had been previously characterized. Heretofore most methods have been concerned with a certain phase of surfactant analysis. It is the purpose of this paper to show how surfactants or actives may be isolated from detergent compositions and then how the actives are separated and characterized as nonionics, sulfonates, sulfates, and hydrotropes.

Surfactant Characterization. The first step in this study was to characterize the surfactants which would be used for preparing detergent compositions for subsequent analysis. The surfactants used were commercial products, and their characterization was carried out as follows.

Water content was determined by ASTM D1568-58T (1). a) Xylene distillation method was run according to Sections 9 to 12. b) Karl Fischer method was run according to Sections 13 to 18 for samples with less than 1.0% water.

Alcohol insolubles, sodium chloride, neutral oil, active content, combining weight, SO_3, and cationic titration were determined by ASTM D1681-59T (2).

Reagent grade boiled isopropyl alcohol (Merck) cut to 95% by volume with distilled water was used in place of ethanol. Actives, especially tallow alcohol sulfate, had better solubility in 95% isopropyl alcohol than in 95% ethanol.