higher solubility of the esters. The amount of the catalyst did not show any appreciable effect on the extent of the isomerization in petroleum ether.

Displacement chromatography in conjunction with ultraviolet and infrared spectra is shown to be an effective means for separation and identification of *cis, trans* diene and triene isomers.

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Detergents from Synthetic Olefins[1]

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OLEFINS synthesized in the Fischer-Tropsch process, although commercially unavailable, are a potential source of raw material for detergents (11). They possess a higher degree of linearity and terminal unsaturation than the olefin polymers from propylene (4) used in the commercial manufacture (6) of alkylaryl sulfonates. Because the hydrocarbon radical provides the hydrophobic part of surface-active agents, the nature of the olefin would be expected to affect detergent performance. In alkyl sulfates, straight-chain nonterminal olefins are known to produce good foaming and wetting properties whereas straight-chain terminal olefins give good detergency (9, 13).

Because of a shortage of natural fats, detergents from Fischer-Tropsch olefins were investigated in Germany during World War II. Although a plant had been constructed to make alkyl sulfates, the war ended and it was never placed in operation (9, 15).

In the course of research on possible uses of Fischer-Tropsch products we have experimentally studied the effectiveness of surface-active agents prepared from such olefins. Sodium alkylbenzene sulfonates and sodium alkyl sulfates were prepared from the olefins containing 11, 12, 13, 14, 15, and 16 carbon atoms. Individual sulfonates and the mixture of 11- through 15-carbon sulfonates corresponding to the distribution of olefins in the Fischer-Tropsch product were evaluated by comparison with a reference sulfonate prepared from propylene tetramer. The individual sulfates and the mixture of 12- through 17-carbon sulfates were evaluated by comparison with a reference sulfate prepared from lauryl alcohol. Conventional soil-removal, whiteness-retention, foaming, and wetting tests were used to estimate relative effectiveness. Observations of caking, hygroscopicity, and solubility were also made.

Preparation

The olefins were synthesized in a pilot plant by the fluidized-iron process (17, 18). Reaction of carbon monoxide and hydrogen at 300° to 340°C. under 15 to 40 atmospheres' pressure gave a liquid product containing a wide molecular-weight distribution of olefins, paraffins, and oxygenated compounds. The product was washed with caustic to remove organic acids and then fractionated. Analysis of the fractions gave the estimated composition shown in Table I. Individual fractions contain 13% to 29% normal terminal olefins whereas the propylene polymer contains very small amounts of such structures (4).

TABLE I

Properties of Olefin Fractions

Fraction	Boiling Range, °C.	Olefin %	Olefin Distribution, %			
			Normal		Branched	
			Terminal	Internal	Tertiary	Others
$C_{11}H_{22}$	174-196	55	29	24	19	28
$C_{12}H_{24}$	196-216	54	25	25	20	30
$C_{13}H_{26}$	216-237	54	21	25	20	34
$C_{14}H_{28}$	237-254	53	17	25	21	37
$C_{15}H_{30}$	254-273	53	16	23	21	40
$C_{16}H_{32}$	273-287	52	13	22	22	43

Alkylbenzenes were prepared from the fractions of 11- through 15-carbon atoms by alkylating benzene with anhydrous ethanesulfonic acid as the catalyst (1). Each alkylate was washed with caustic and fractionated to give a center cut for sulfonation. Physical properties of these center cuts are listed in Table II.

TABLE II

Physical Properties of Alkylbenzenes

Alkylbenzene	Boiling Range, °C., 5 mm.	N_D^{20}	Specific Gravity 25°C.
$C_{11}H_{23}C_6H_5$	115-135	1.4863	0.873
$C_{12}H_{25}C_6H_5$	135-150	1.4871	0.878
$C_{13}H_{27}C_6H_5$	150-165	1.4926	0.890
$C_{14}H_{29}C_6H_5$	165-175	1.4875	0.894
$C_{15}H_{31}C_6H_5$	175-185	1.4848	0.883

Each was sulfonated with 100% sulfuric acid (10), neutralized with sodium hydroxide, deoiled, desalted, and dried.

Sodium alkyl sulfates were synthesized from alcohols obtained by the classical oxo reaction (8, 12, 14). The mixture of alcohols contains one more carbon atom than the starting olefins. Crude alcohols were fractionated to give center cuts with the properties listed in Table III. Each center cut was sulfated with chlorosulfonic acid (5) in absolute ether. Neutralization of the sulfates with sodium hydroxide was followed by deoiling, desalting, and drying.

For each detergent type a reference standard common to the trade was prepared in the same way as the experimental samples. A sodium dodecyl sulfonate was prepared from propylene tetramer. A sodium lauryl sulfate was prepared from lauryl alcohol melting at 23° to 24°C.

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TABLE III

Properties of Oxo Alcohols

Alcohol	Boiling Range, °C., 5 mm.	N_D^{20}	Specific Gravity 25°C.	Normal Isomer, Weight %
$C_{12}H_{25}OH$	164-179	1.4489	0.849	22
$C_{13}H_{27}OH$	163-180	1.4510	0.862	15
$C_{14}H_{29}OH$	172-194	1.4548	0.868	13
$C_{15}H_{31}OH$	183-209	1.4594	0.848	18
$C_{16}H_{33}OH$	192-221	1.4639	0.895	25
$C_{17}H_{35}OH$	203-233	1.4640	0.883	23

Evaluation

Surface-active properties were evaluated by four conventional laboratory tests:

Whiteness retention (16) was determined by measuring the decrease in light reflectance of unsoiled cotton swatches after agitation in the detergent solution containing water-dispersed carbon black for 15 min. in the Atlas Launder-O-Meter at 140°F.

Soil removal (7) was determined by measuring, with the Hunter Multipurpose Reflectometer, the increase in light reflectance after a 20-min. wash in the Launder-O-Meter. Cotton cloth soiled with lampblack, mineral oil, and hydrogenated vegetable oil was washed at 140°F. Wool cloth soiled with lampblack, mineral oil, and tallow was washed at 110°F.

Foaming properties were measured by the Ross-Miles test at 25°C. (3).

Wetting ability was measured by the Draves-Clarkson Cotton Skein test (2).

Measurements were made in water at three concentration levels of active ingredient: 0.2, 0.1, and 0.05% by weight. The water contained 176 p.p.m. of hardness with a ratio of calcium to magnesium of 60 to 40. In all cases two parts of sodium sulfate were present for each part of detergent. The pH of the solutions was between 6.5 and 8.0.

Measurements of hygroscopicity, caking, rate of solution, and solubility were made to estimate the physical performance of the dried products.

Sodium Alkylbenzene Sulfonates

These tests were used to compare the effectiveness of the sulfonates, the mixture, and the reference sulfonate. Figure 1 illustrates the effect of alkyl carbon number and concentration of active ingredient on soil removal from cotton, foaming properties, and wetting ability. Whiteness retention was good for all the products; the 13-carbon sulfonate was better than the reference sulfonate.

In soil removal from cotton the 13- and 14-carbon sulfonates are the best members of the series. Both are superior to the reference sulfonate. The mixture is as effective as the better individual products and loses little in detergency by inclusion of the less-effective members. In soil removal from wool the 11- through 13-carbon sulfonates were equal to the refererence sulfonate and the 14- and 15-carbon sulfonates were superior.

In foaming properties the 11-carbon sulfonate, the best of the series, is more effective than the reference sulfonate; the mixture is equivalent.

In wetting ability the 11- and 12-carbon sulfonates are better than the reference sulfonate. The mixture and the 13-carbon sulfonate are equivalent, and the 14- and 15-carbon sulfonates are poorer.

Samples of all the sulfonates were drum-dried with sodium sulfate to a composition of 40% detergent and 60% sodium sulfate. All of them were more soluble than the reference sulfonate. On exposure to 80% relative humidity at 90°F. the sulfonates were more resistant to caking and moisture pickup.

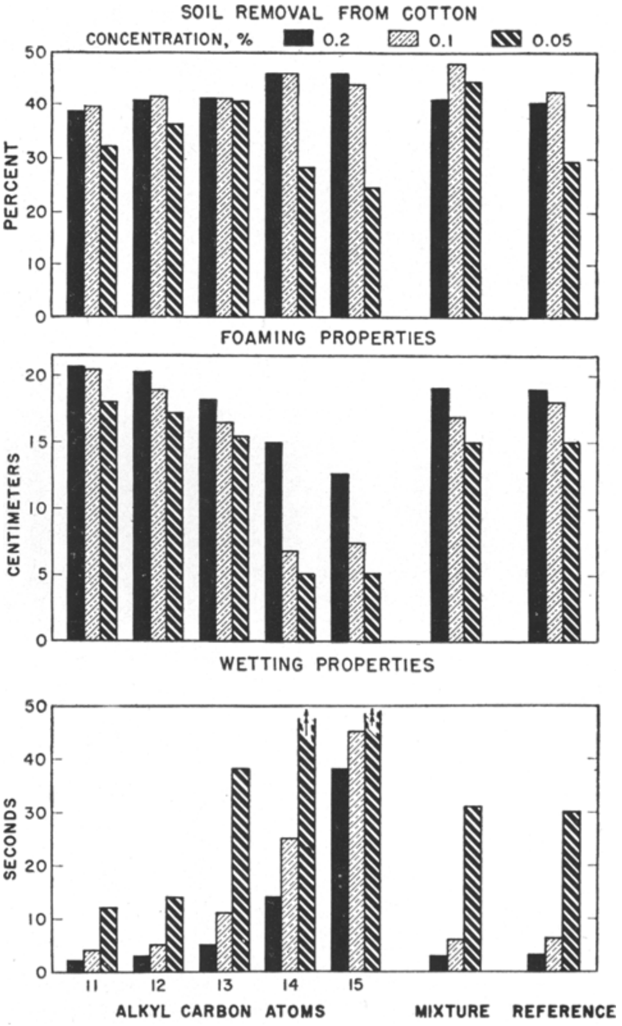

FIG. 1. Surface activity of alkylbenzene sulfonates.

Sodium Alkyl Sulfates

The effectiveness of sulfates, the mixture, and the reference sulfate was determined by the same tests. Figure 2 illustrates the effect of alkyl carbon number and concentration of active ingredient on soil removal from cotton, foaming properties, and wetting ability. Whiteness retention improved with increasing alkyl size; the 16- and 17-carbon sulfates were the best. The 14- through 17-carbon sulfates were more effective than the reference sulfate.

In soil removal from cotton the 16- and 17-carbon sulfates are slightly better than the mixture, which is somewhat more effective than the reference sulfate. In soil removal from wool the 16- and 17-carbon sulfates were far superior to the reference sulfate and to the mixture.

In foaming properties the 13-, 14-, and 15-carbon sulfates, as well as the mixture, are equivalent to the reference sulfate at 0.2 and 0.1% concentrations and superior at 0.05%. In wetting ability the 13- through 16-carbon sulfates and the mixture are more effective than the reference sulfate.

All the alkyl sulfates, drum-dried to a composition of 40% sulfate and 60% sodium sulfate, were waxy; the reference sulfate was friable. All the products were white. On exposure to 80% relative humidity at 90°F. the alkyl sulfates were less resistant to cak-

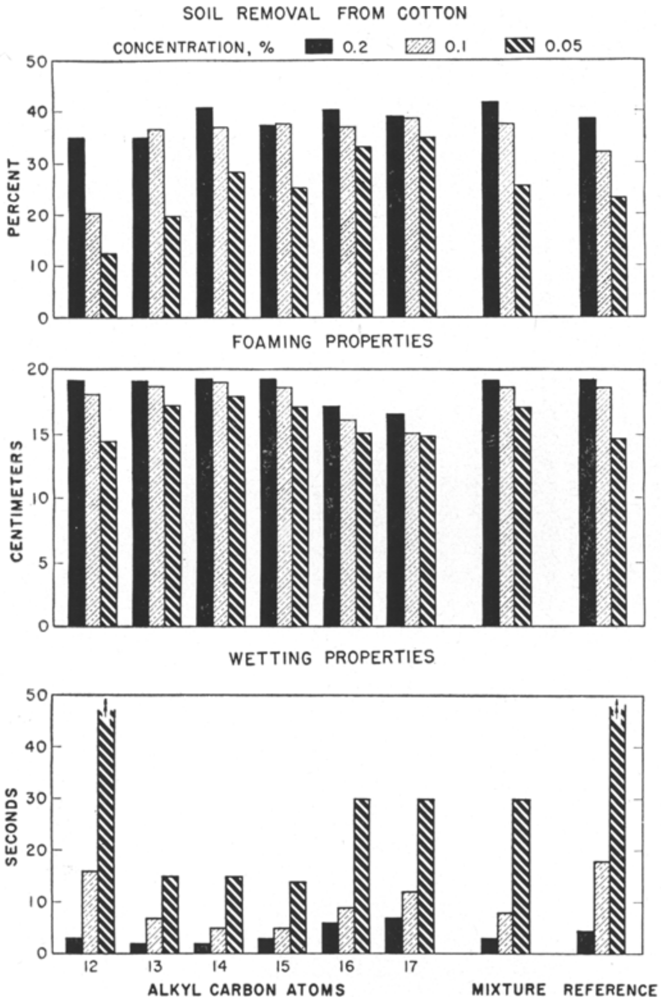

FIG. 2. Surface activity of alkyl sulfates.

ing and moisture pickup than the reference sulfate. However they were equivalent to a commercial sample of coconut fatty-alcohol sulfate.

Conclusion

Detergents prepared from Fischer-Tropsch olefins are thus measurably better than the reference standards prepared from propylene tetramer or lauryl alcohol. The combination of straight and branched chains with both terminal and internal double bonds produces the high level of surface activity found with these synthetic olefins.

Although the optimum molecular weights for the experimental sulfonates are about the same as for sulfonates from polymer olefins, the surface activity is somewhat better. In physical properties these sulfonates are superior to polymer-olefin sulfonates in resistance to caking and in rate of solution. The optimum experimental sulfates, of 14- through 16-carbon atoms, are superior to lauryl sulfate. The branched structure of these alkyl sulfates probably gives rise to their soft, waxy, and hygroscopic character. Total mixtures of these experimental products are better than the respective reference standards.

Both types of detergents prepard from Fischer-Tropsch olefins are about equivalent. The alkylbenzene sulfonates appear to be superior to similar products now in every-day use. Although Fischer-Tropsch olefins are a promising source of raw material for detergents, there is no assurance that they will be commercially available in the near future.

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Alcoholic Extraction of Vegetable Oils. I. Solubilities of Cottonseed, Peanut, Sesame, and Soybean Oils in Aqueous Ethanol

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THE MOST commonly used solvents for the solvent extraction of vegetable oils in the United States are low boiling petroleum fractions, such as normal hexane. In European countries benzene, trichloroethylene, and cyclohexane have been used. Considerable work has been done on the utilization of ethanol and isopropyl alcohol as solvents in this country. Beckel and co-workers developed a continuous non-distillation method for extraction of soybean oil, which theoretically requires only 7/10 of the energy required by the hexane process (1). Ethyl alcohol is said to produce a meal having a higher nutritive

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