period of time. Evidently the process of *trans*-isomerization did not continue in the irradiated solutions.

Summary

The oleic acid of IV 89.2 was irradiated with cathode rays at doses of 15 x 10^6 to 70 x 10^6 rep and was found to have been *trans*-isomerized from 2.5% at 45 x 10^6 rep to 9.4% at 70 x 10^6 rep; the oleic acid of IV 89.8 irradiated at doses of 13.4 x 10^6 to 401.6 x 10^6 rep and was found to have been *trans*-isomerized to 4.9% at 187.4 x 10^6 rep and to 14.6% at 401.6%.

The *trans*-isomerization was independent of oxygen.

Aqueous solutions of potassium oleate at 1% concentration were irradiated with doses from 1 x 10^6 rep to 5 x 10^6 rep. The oleic acid recovered from the irradiated solutions was found to have been *trans*-isomerized from 8.1% at 1 x 10^6 rep to 1.9% at 5 x 10^6 rep; the oleic acid recovered from the 2.5% solutions was found to have been *trans*-isomerized to 8.3% at 5 x 10^6 rep, 11.9% at 10 x 10^6 rep, and 0.1% at 30 x 10^6 rep.

A modified "baseline" technique in infrared spectrophotometric analysis is described.

Acknowledgments

Appreciation is expressed to J. G. Trump and K. A. Wright of the Electrical Engineering Department, M.I.T. for the irradiation of samples with cathode rays from the 3 M.e.v. Van de Graaff accelerator.

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An Evaluation of the Detergency Value of a Series of Alkylbenzene Sulfonates by Ultrasonic Technique

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IN THIS STUDY ultrasonic energy has been used in the direct evaluation of the detergent characteristics of a series of highly purified sodium alkylbenzene sulfonates which have been synthesized in these laboratories. In a previous paper Sherrill and White (3) presented preliminary results on studies of the magnitude of forces binding soils to textile surfaces. In these studies an ultrasonic cone transducer was used as a means of providing mechanical action of a precisely controlled magnitude. It was demonstrated that specific energy requirements prevail for any given level of soil removal. It also was pointed out that greater precision and reduced test-time was possible through the use of this technique.

The use of synthetic detergents in this country has grown remarkably over the past 30 years. The sodium alkylbenzene sulfonates have played an important role in the development of synthetic detergents. Currently the higher alkylaryl sulfonates account for the largest tonnage of synthetic surface-active agents in this country (2). Accordingly a study of the relationships of the structure of the molecule to detergency should be of interest and value to the industry.

One extensive study in this field has been made by Kourtz (1), in which the relationship of the surface activity and number of carbon atoms in the alkyl group of certain alkylbenzene sulfonates was reported. This investigator found from surface and interfacial tension measurements that, in general, the surface activity increased with an increase in the length of the alkyl chain in the alkylbenzene sulfonate.

In this study 17 alkylbenzene sulfonates were prepared, containing six to 18 carbon atoms. Compounds containing 13, 15, and 17 carbons in the alkyl group were not synthesized. These syntheses made it possible to compare straight-chain, branch-chain, and cyclic compounds as regards detergency efficiency.

Experimental Procedure

Preparation of Alkylbenzene Sulfonates. The 17 alkylbenzene sulfonates synthesized included four compounds containing six carbon atoms in the alkyl radical, one with seven carbons, two with eight carbons, one with nine carbons, two with 10 carbons, one with 11 carbons. two with 12 carbons, two with 14 carbons, one with 16, and one with 18 carbons in the alkyl radical.

In general, the preparation of the alkylbenzene sulfonates included the following series of conversions: acid to acid chloride, to alkylaryl ketone, to hydrazone of the ketone, to alkylbenzene, to sodium alkylbenzene sulfonate.

A total of 10 of the 17 sodium alkylbenzene sulfonates had straight-chain alkyl groups. The alkylbenzenes were not synthesized directly by the Friedel-Crafts reaction since the reaction product would undoubtedly have contained a mixture of straight- and branch-chain alkyl groups which are not readily sep-

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arated. The preparation of the alkyl phenyl ketone was accordingly carried out, using an acyl halide and benzene, followed by reduction of the ketone by the Wolff-Kishner reaction, in order to arrive at the desired alkylbenzene. The alkylbenzene was sulfonated readily, and the sodium alkylbenzene sulfonate was isolated.

A total of five branch-chain alkylbenzenes were prepared in the course of this study which had not previously been reported in the literature. The boiling point and refractive indices of these hydrocarbons are shown in Table I. The properties of the remaining 12 compounds conformed closely to values extant in the literature and need not be listed at this point.

TABLE I
Physical Properties of Five Branch-Chain Alkylbenzenes

Compound	Boiling point, °C./1 mm.	Refractive index, n_D^{20}
1. 2-ethylbutylbenzene..........	68–69	1.4959
2. 2-ethylhexylbenzene..........	67.5–70	1.4880
3. 2-ethyloctylbenzene..........	94–95	1.4857
4. 2-ethyldecylbenzene..........	122–125	1.4850
5. 2-ethyldodecylbenzene......	134–137	1.4840

Ultrasonic Transducer. The device used for determining soil-removal potentialities of the compounds synthesized in this study was a dynamic detergency tester, the central feature of which is an ultrasonic transducer in the form of a truncated cone designed and built by the Clevite-Brush Development Company and adapted in these laboratories for the purpose of removing soil from standard soil fabrics in a short time. An electronic driver with self-contained, automatic frequency control serves to drive the cone. Power input to the cone is measured by means of a volt-ampere-watt meter. The cone transducer operates at about 46 kilocycles per second with maximum power input of about eight watts.

Calculation reveals the relationship of power output to power input. A power input of seven watts, for example, generates a displacement amplitude of 10.8 microns, equivalent to 0.158 watts output.

The energy output can be related to soil removal from an exposed surface. Highly precise results may be obtained in a relatively short time through the use of the cone transducer, in comparison with data obtained using mechanical washers of the laboratory or commercial type.

The ultrasonic cone transducer in use is supported above and in contact with standard soil fabric, which is mounted on a turntable immersed in the detergent liquor under test. The turntable rotates 70 r.p.m., and the cone is moved across the fabric surface, giving rise to a cleaned, circular area of fabric about three inches in diameter (which is sufficient to cover the opening of a Hunter Multipurpose Reflectometer). The device is shown schematically in Figure 1 and has been described in detail by Sherrill and White (3).

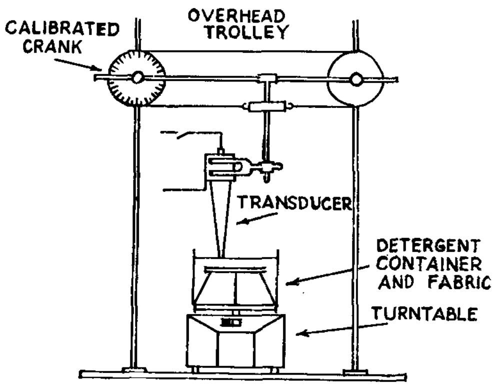

FIG. 1. Schematic diagram of dynamic detergency tester.

A test period of 650 revolutions of the turntable corresponds to 9.39 min. At a power input of 7.0 watts, power output amounts to about 0.158 watt. Each swatch therefore is subject to 89 watt-seconds (joules) of mechanical energy, distributed over a surface area of 8.95 square inches.

Standard Soil. This has been described in detail by Sherrill and White (3) and comprises a black-fat-oil suspension applied to Indian Head fabric by immersion. The fabric is carefully standardized in terms of initial reflectance and ease of washback prior to use.

Soil removal was computed, using the equation of Lambert, as follows:

$$(R_x - R_s / R_o - R_s) \times 100 = \text{percentage soil removal}$$

where R_x = reflectance of washed sample
R_s = reflectance of unwashed standard soil
R_o = reflectance of unsoiled fabric

Reflectance was determined by using a Hunter Multi-Purpose Reflectometer with a green filter (5550 ±1000 Å).

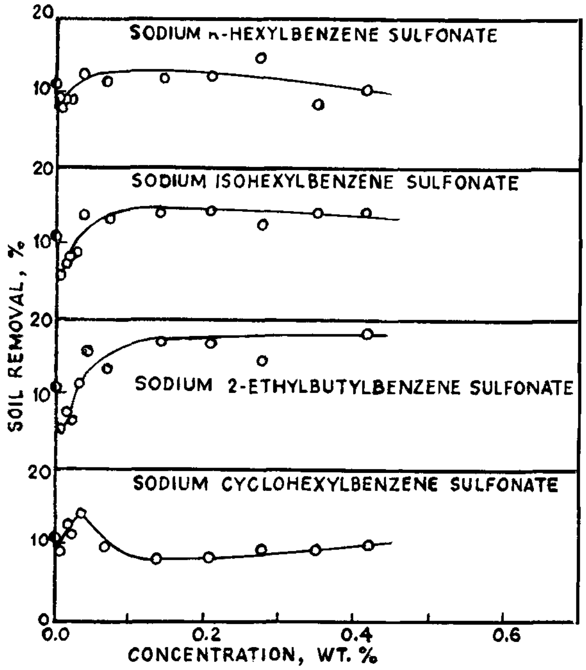

FIG. 2. Soil-removal efficiency of sodium hexylbenzene sulfonates.

Results

The soil-removal studies involving 17 carefully synthesized alkyl aryl sulfonates are shown in Figures 2 through 6 for concentrations ranging upwards of 0.5 weight percentage for each compound.

The Six-Carbon Alkylbenzene Sulfonate Isomers. Results on these compounds are summarized in Figure 2. There is little difference in soil-removal efficiency among the four isomers: sodium n-hexyl-, isohexyl-, 2-ethylbutyl-, and cyclohexylbenzene sulfonate. All

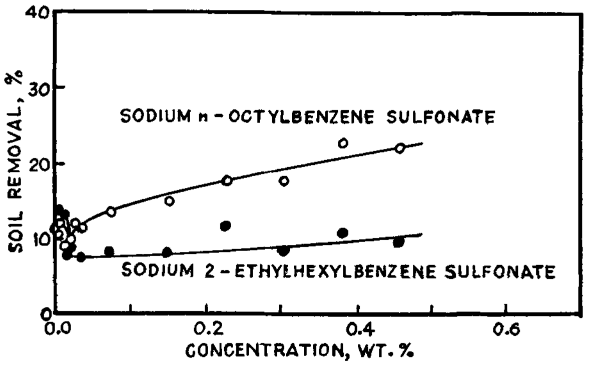

Fig. 3. Soil-removal efficiency of sodium octylbenzene sulfonates.

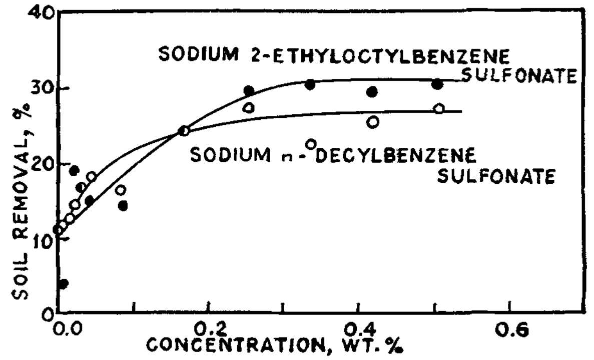

Fig. 4. Soil-removal efficiency of sodium decylbenzene sulfonates.

showed minima in the early concentration range. Not any of the four compounds produced soil removal in excess of 18%, which is not notably higher than the 11% recorded for distilled water using this soil cloth.

The Eight-, Ten-, Twelve-, and Fourteen-Carbon Straight- and Branch-Chain Compounds. Data on these compounds are shown in Figures 3, 4, 5, and 6.

The straight-chain compound in three of four cases exhibited greater soil-removal efficiency than the branch-chain isomer in all cases save for the 10-carbon alkyl residue compound, where sodium 2-ethyloctylbenzene sulfonate was more effective above a concentration of about 0.2 weight percentage. At this point the low concentration minima in soil-removal concentration curves disappear with the straight-chain compounds but persist upwards to the 12-carbon alkyl residue compound in the branch-chain series.

The growth type of curve becomes more pronounced with increasing chain length, becoming fully evident with sodium n-tetradecylbenzene sulfonate.

The Straight-Chain Alkylbenzene Sulfonates. The soil removal-concentration functions of 10 straight chain sodium alkylbenzene sulfonates having six to 18 carbon atoms in the alkyl residue all are shown on Figure 7. The development of detergent power and limitations of solubility are at once evident from examination of these data. Note that the six- and seven-carbon alkyl group compounds reveal minima at low concentrations. The eight- and nine-carbon alkyl group compounds yield relatively linear functions for soil removal *versus* concentration over the bulk of the concentration range. Compounds having 10 to 16 carbons in the alkyl residue show increasingly greater growth-curve tendency.

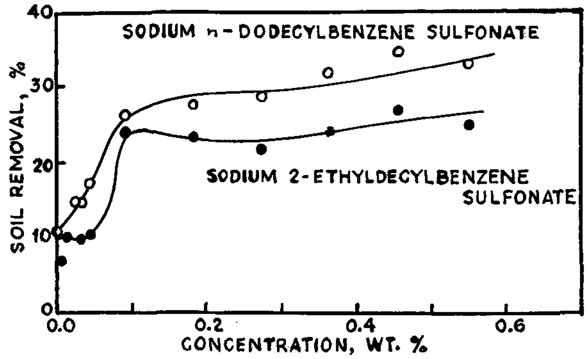

Fig. 5. Soil-removal efficiency of sodium dodecylbenzene sulfonates.

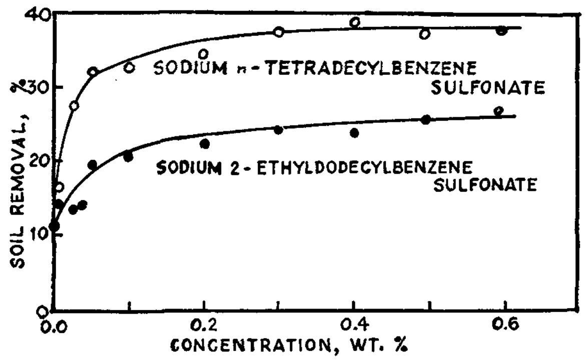

Fig. 6. Soil-removal efficiency of sodium tetradecylbenzene sulfonates.

Although the 16-carbon, alkyl-group compound shows a steeper rate of increase of soil removal with concentration than the 14-carbon compound, the latter detergent does not achieve the level of soil removal of the former at any concentration. Reduced solubility appears to be responsible for this, as is borne out by the fact that sodium n-octadecylbenzene sulfonate produces much lower soil removal than sodium n-tetradecylbenzene sulfonate.

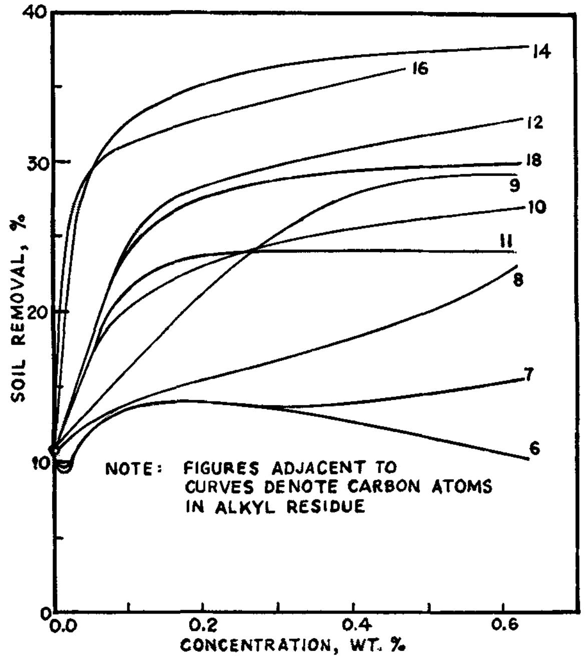

Fig. 7. Soil-removal efficiency of straight-chain sodium alkylbenzene sulfonates.

Summary

The soil removal efficiency of 17 sodium alkylbenzene sulfonates having alkyl residues ranging from six- to 18-carbon atoms, which have been synthesized and purified especially for this work, has been described. Evaluation has been accomplished by means of an ultrasonic cone transducer capable of producing mechanical action of a very highly reproducible character and at a measurable rate of expenditure of energy. Compounds having straight-chain alkyl residues produce generally greater detergency efficiency than the branch chain homolog. Detergent character becomes pronounced at about 10 carbon atoms in the alkyl residue, but detergency is diminished above about 14 to 16 carbon atoms in the alkyl group because of reduced solubility.

Acknowledgments

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Slurry Storage of Light Soda Ash[1]

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LIGHT SODA ASH or sodium carbonate is a fluffy, dusty hygroscopic material with an angle of repose that sometimes exceeds 50 degrees. With increased use in the chemical, oil, non-ferrous metal, and pulp and paper industries, production of this basic chemical has climbed to about five and one-half million tons per year. This consumption could add up to a lot of headaches for the people who handle and store the onerous compound. This paper will deal with a recent development in storing soda ash as a slurry and with an economical, pneumatic unloading system adapted to this type of storage. The systems are of particular interest to those who use soda ash in a solution form.

Pilot Plant

The principle of converting dry sodium carbonate into a storable slurry has been known for years. It is merely one of transforming dry soda ash with a bulk density of 35 lbs. per cubic foot into a wet sodium carbonate monohydrate with a density of 56 lbs. per cubic foot. It was not until recent years that this principle was fully exploited and a practical system for storing soda ash as a monohydrate slurry was perfected.

Extensive research has been carried out to establish the basic data needed for the design and operation of a pilot-plant unit.

The large-scale work was carried out in a 5,000-gal. steel tank 9 ft. in diameter by 11 ft. high. The tank was equipped with a sparger or dissolving arrangement containing 11 check-valve type of nozzles. A screw conveyor discharging into a sluiceway or chute was used to charge the tank with soda ash. A pump circulated solution into the ash-charging chute to dissolve and wash soda ash into the tank. The suction hose of the pump was maintained just below the liquor surface to avoid circulating any solid particles of ash. Later the tank was equipped with a floating suction and swing joint, as shown in Figure 1.

Prior to the initial unloading the tank was charged with a predetermined quantity of water. As soda ash was added to the water, the resultant solution increased in concentration until it reached saturation. Saturated solution was then used to wet the incoming ash, and monohydrate was formed by both crystallization from the saturated solution and hydration of dry soda ash. The monohydrate formed was dense and settled rapidly, making available a clear saturated solution for recycle. Loading of the tank was continued until approximately 92% of its volume was composed of slurry. Dissolving of the monohydrate slurry was accomplished by introducing a metered water flow through the sparging nozzles.

Design Data

Preliminary design data for a commercial installation were determined from the pilot plant (Table I).

The slurry storage tank should be kept at 105°F. or above to avoid formation of heptahydrate and decahydrate. The hydrates of 7 and 10 moles of water have negative heats of solution of 178 and 270 Btu. per pound of sodium carbonate, respectively, and are difficult to dissolve. The monohydrate, with a positive heat of solution of 42.5 Btu., dissolves quite easily.

A considerable amount of heat is evolved in the charging process because of the heats of solution and monohydration. In the transition from water to a slurry occupying 92% of the tank volume, a tempera-

MECHANICAL PILOT PLANT

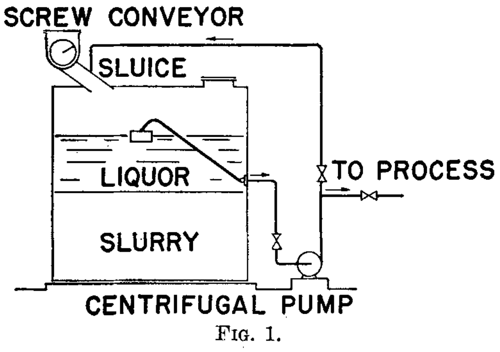

FIG. 1.

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