TABLE IV
Chromatograms of Alkylbenzenes

Sample	A	B	C	D	Reference
Detergency	Good	Bad	Bad	Good	Good
Peak #					
1	21.8	20.9	19.3	24.2	25.6
2	18.8	21.0	19.7	21.5	17.4
3	11.6	13.1	11.3	14.1	9.8
4	14.1	19.1	19.4	15.7	16.2
5	4.1	5.0	5.3	3.3	3.9
6	11.7	11.5	12.5	9.6	11.3
7	9.2	6.1	7.4	6.6	6.0
8	5.2	2.1	3.3	2.9	5.6
9	3.5	1.2	1.8	2.0	4.2
$\Sigma\ \sigma$ Method I	+1.13	+1.68	+3.63	−1.75	0
$\Sigma\ \sigma$ Method II	+2.08	+2.99	+4.48	−0.83	0

tion contain some dangers, since big positive deviations can be cancelled out by big negative deviations; therefore, it was preferable to compare individual peaks, particularly the ratio of the first two peaks as well as the No. 4 peak, as described earlier.

It was concluded from these correlations that some quite minor variations in the nature of the alkylbenzene sulfonate, not detectable by standard analytical techniques, could greatly affect detergency. This gas chromatographic technique of checking the alkylbenzene sulfonates can be used effectively to assure both the quality and the standard of a particular formulation, as well as product uniformity.

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Identification of Soapstocks by Gas Chromatographic Techniques[1]

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The stock of a given soap may be estimated when the ratios of the fatty acids present are known. A new gas chromatographic procedure utilizing a novel automatic attenuator is presented. The samples are prepared by refluxing the soap with a methanolic solution of boron trifluoride and separating the esters so formed by standard gas-liquid chromatographic procedures. Soapstock compositions are determined by comparison with reference curves.

THE STOCK of a given soap may be determined if the fatty acid composition is known. This is accomplished in many laboratories by performing a number of average physical and chemical measurements such as titer, saponification value, and iodine number (1). These measurements fail to give a complete picture when the soapstock has been partially hydrogenated, when different sources of tallow are employed, and when blends containing other than tallow and coconut are utilized. In addition, the above mentioned measurements are time consuming. Primarily, tallow is a triglyceride of stearic, oleic, and palmitic acids; coco is a triglyceride of lauric and myristic acids.

Gas-liquid chromatography of fatty methyl esters have been widely reported in the literature (2, 4, 5). More recently chromatographic separation of fatty acids has been accomplished without preparation of the corresponding methyl esters (8). The quantitative relationship of individual peak areas and composition of fatty methyl ester chromatograms is also well documented (3, 6, 7). Utilizing an instrument equipped with a novel automatic attenuator, the techniques of gas-liquid chromatography have been applied to the study of soapstocks.

Experimental

Reagents. (1) Boron trifluoride in methanol, prepared by dissolving 120 g. of boron trifluoride in 1 l. of methanol. The solution requires refrigeration. (2) One g. of sodium metal dissolved in 10 ml. of methanol. This solution is unstable and needs to be prepared daily.

Instrument. Laboratory-built chromatograph, utilizing a Leeds and Northrup recorder, with Gow-Mac thermal conductivity cell.

Sample Preparation. Soap samples to be chromatographed are first warmed with 6% sulfuric acid. The fatty acids so liberated are then heated with an equal volume of warm boron trifluoride in methanol according to the method of Metcalfe, *et al.* (9). The esters which form are insoluble in water and float to the top. Washing is unnecessary and separation may be accomplished with the aid of a separatory funnel. If analyzing the soap feed stock instead of the soap, that is triglycerides, esterification is accomplished by refluxing with freshly prepared sodium methoxide.

Chromatographic Conditions. The fatty methyl esters are chromatographed under the following conditions:

Column temperature	200°C.
Column packing	Craig polysuccinate
Column length	5 feet
Column diameter	¼ in. O.D.
Carrier gas	Helium
Carrier gas flow rate	100 ml./min.
Preheater temperature	250°C.
Detector	Gow-Mac Model TE II
Recorder	Leeds and Northrup Speedomax G

Results and Discussion

The Instrument. To get a true insight into the composition of soapstocks, attention must be paid to both minor and major peaks. To accomplish this, the gas chromatographic instrument must couple sensitivity with attenuation so that all peaks, whether major or minor, are shown in proper relation on the same chart paper. For this purpose a decimal attenuator was constructed, the details of which are shown in Fig. 1.

The heart of the attenuator is the four-gang Uniselector switch, manufactured by the General Electric Co., of England. Gang one of the switch contains

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[1] Presented at Spring Meeting, American Oil Chemists' Society, St. Louis, Missouri, May 1–3, 1961.

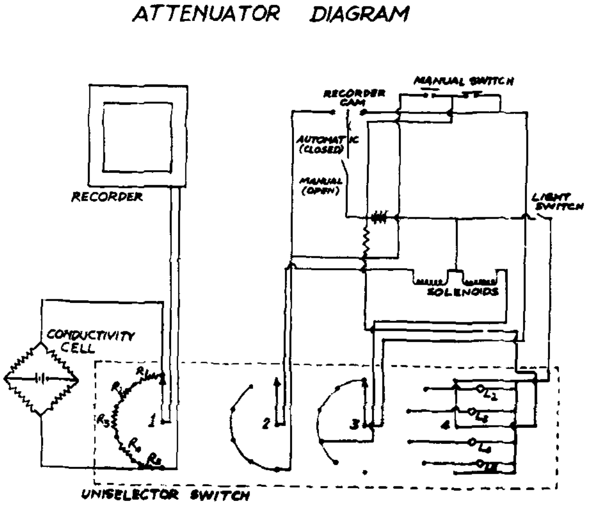

Fig. 1. Electrical diagram of automatic attenuator.

precision resistors numbered R_1 through R_5. The values of these determine the signal suppression at any corresponding contact and, in this case, are multiples of ten of each other thereby causing attenuation to follow a decimal pattern. The sum of values of all of the resistors equals the input impedance of the recorder used. Gang two controls the clockwise rotation of the switch arms, which results in lesser amounts of attenuation. The most clockwise position of this gang is not wired to prevent the switch from moving below zero attenuation and losing its signal. Gang three controls upscale movement, and here the most counter-clockwise contact is not wired to prevent the switch from losing the signal on its high end. The contacts of gang four are wired to corresponding dial lights. These show which range or scale is functioning. The base scale, with zero attenuation, is not wired with an indicator light to save battery current since, most of the time, the instrument operates on base range. The actual changing of ranges is accomplished by means of two solenoids in the switch: one to shift downward and the other to shift upward. These can be actuated by cams on the slidewire shaft of the recorder or they may be operated manually. The signal from the attenuator is recorded by a Leeds and Northrup one-second one-millivolt Speedomax G recorder. The signal to the attenuator is furnished by a Gow-Mac model TE II thermal conductivity cell carrying 250 milliampere current.

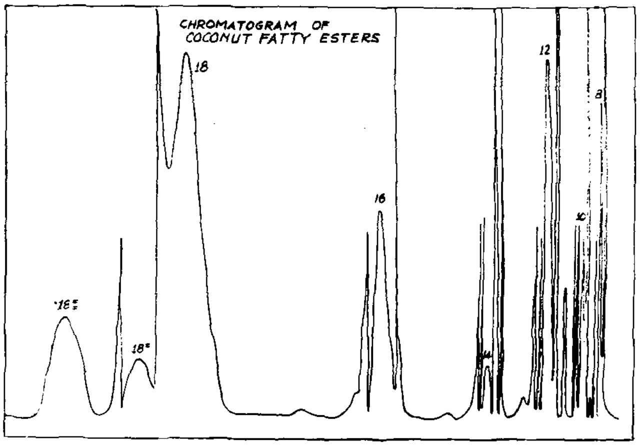

Fig. 2. Typical chromatogram of coconut fatty esters.

Typical Pattern. Fig. 2 shows a typical chromatogram, this one being of coconut fatty esters. The range of the instrument at any time can be determined by counting the number of times the recorder pen hits the top of the chart. Each time the attenuator switch is activated, the signal to the recorder is divided by 10, on rising voltage, and multiplied by ten on lowered signal. This not only reproduces major peaks but trace compounds are also shown.

Tallow Sources. Tallows vary slightly depending upon their source and prior treatment. This results in changes in the amount of some minor components a fact which is readily apparent from the chromatogram. For instance, the tallow shown in Fig. 3 contains 0.25% C-8 fraction, 0.35% C-10 fraction, and 2.5% C-12 fraction. Tallow from a different supplier run concurrently showed no C-8 or C-10 and only 0.75% C-12 fraction. Differences can usually be seen in the amount of myristoleic and palmitoleic fractions also. Although tallows do vary slightly, the tallow from any given source is quite consistent and characteristic of its source.

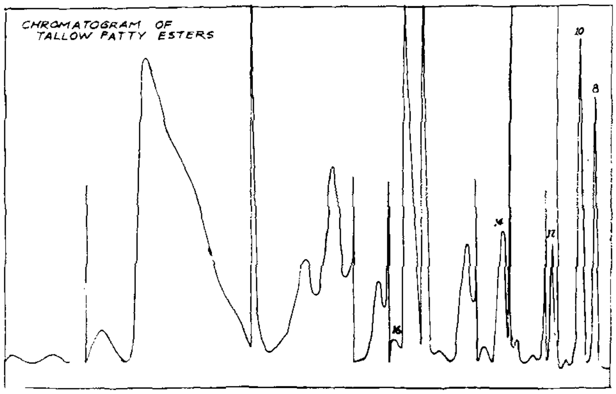

Fig. 3. Typical chromatogram of tallow fatty ester.

Mixtures Investigated. Fourteen different synthetic mixtures were compounded from the methyl esters of tallow-coconut fatty acids. In addition, a number of tallows from different sources, both domestic and foreign, have been characterized The chromatograms of these tallows and blends serve as reference patterns to which chromatograms of unknown soapstock esters may be compared. With the aid of these reference patterns, an insight to the composition of a given soapstock can at once be seen. A typical chromatogram of tallow-coconut fatty esters is reproduced in Fig. 4. The peaks due to myristoleic, palmitoleic, and also smaller peaks due to trace amounts of odd carbon number esters, all come from the tallow. This particular pattern is for an 85–15 tallow-coconut mix. The dotted lines indicate the position of the peak if the mixtures were in the ratio of 75–25 tallow-coconut fatty esters. For a 10% change in ratio, the C-16 and C-18 peaks change but little. The C-14 peak is measurably higher in the 75–25 chromatogram; the C-12 peak appears to rise less than the C-14, but this is on the ten-fold higher scale and, if in the base range, would be 13 chart widths longer. The dotted C-10 peak appears below the one for the 85–15 ratio pattern; actually the recorder pen, if on the base scale, would have gone off the edge of the chart and a third of the chart width more.

Comparison of Unknown Pattern. Fatty esters from an unknown soap bar may be chromatographed as already outlined. The pattern obtained may then be

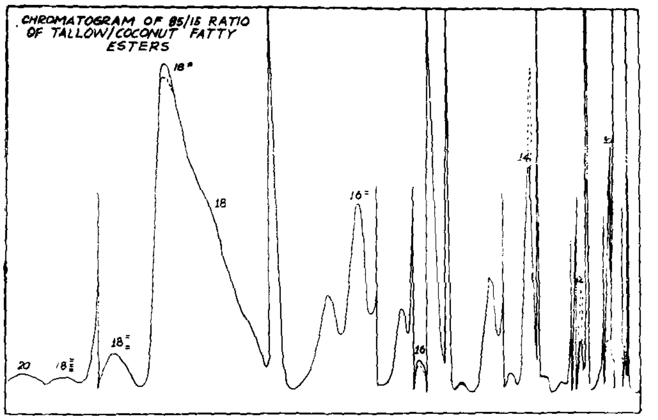

FIG. 4. Chromatogram of 85/15 ratio of tallow/coconut fatty esters with 75/25 ratio superimposed.

compared with a standard pattern and the closest one selected. Confirmation may be obtained by running the unknown sample and a standard mix on the same chromatogram using different colored inks.

Summary

1) In tallow-coconut soapstocks vapor-phase chromatographic techniques are superior in accuracy and less time-consuming than conventional physical-chemical methods.

2) For stocks containing other than tallow and coconut base, or where partial hydrogenation has been carried out, vapor-phase chromatography gives a more complete picture.

3) Vapor-phase chromatography gives indications of the source and/or prior treatment of a given stock.

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Sodium Alkyl *a*-Sulfopelargonates, $C_7H_{15}CH(SO_3Na)CO_2R$. Wetting and Related Properties[1]

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A series of sodium alkyl α-sulfopelargonates prepared from sodium α-sulfopelargonic acid and alcohols of from 2 to 12 carbon atoms were examined for surface active properties. Esters with the hydrophilic portion in the middle of the molecule, as in sodium hexyl, heptyl, octyl, capryl (or 2-octyl) and 2-ethylhexyl α-sulfopelargonate were very efficient wetting agents with good foaming properties and a c.m.c. of from 2 to 7 millimoles per liter. The presence of the α-sulfo group inhibits hydrolysis of the ester linkage, apparently by steric hindrance. Sodium capryl α-sulfopelargonate, an ester of a secondary alcohol, was particularly stable to acid and alkaline hydrolysis. The esters are easily soluble in water, organic solvents and mineral oil.

ANIONIC SURFACE ACTIVE AGENTS may be expected to be wetting agents rather than detergents when the hydrophilic group is at or near the middle of a hydrophobic chain. The surface active agents are then considered to be oriented at the air-water interface as folded molecules with the hydrophilic group directed downward into the aqueous phase; a structure which in a series of compounds of the same chain length may lead to lower surface and interfacial tension, smaller micelles and higher critical micelle concentration. Sodium heptadecyl 9-sulfate (5) and the branched chain secondary alkyl sulfates (13) and sodium alkyl sulfosuccinates (1), which are important commercial wetting agents, have this relation between the hydrophilic and hydrophobic portions of the molecule.

In a previous report (12) it has been shown that sodium α-sulfopelargonic acid displays little evidence of surface active properties but becomes an efficient wetting agent upon esterification with n-octanol to form sodium octyl α-sulfopelargonate,

$$CH_3(CH_2)_6CH(SO_3Na)CO_2(CH_2)_7CH_3,$$

a compound with the hydrophilic portion at about the middle of the molecule and with hydrophobic alkyl groups of about equal chain length.

The present report concerns the preparation of a series of sodium alkyl α-sulfopelargonates and an investigation of properties, particularly in terms of the structure associated with best wetting characteristics. Further study of these and related esters is projected.

Synthesis

The individual normal primary, secondary, and branched chain primary alcohols of Table I were of standard laboratory quality, rectified by distillation as required. The "oxo" decyl alcohol (Enjay Chemical Co.) is a product from the oxo process, a mixture of 10 carbon atom primary alcohols, predominantly trimethylheptanols. The fluoro alcohol (E. I. du Pont de Nemours & Co., Inc.) is a technical product from the free radical telomerization of tetrafluoroethylene with methanol; the subscript 3 is an average number.

The esters of Table I were conveniently prepared by the same general method, esterification of sodium α-sulfopelargonic acid with a 10% excess of the particular alcohol, in the presence of sulfuric acid as the catalyst, and toluene to remove water of esterification, azeotropically. The following example illustrates the method. Analyses for Na and S agreed with

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