as the production of fatty esters of furfuryl alcohol, the ester interchange method is indispensable. Furfuryl alcohol resinifies in the presence of acids, but its esters may be produced by interchange using alkaline catalysts.

The potential uses of the monohydric alkyl fatty esters are not yet fully realized, but there are many indications that these products may become commercially important in the post-war period. Their use in soap-making will depend in part on the importance to the manufacturers of taking advantage of the possibilities of speeding up the soap-making process by replacing present equipment with new apparatus. The process as ultimately developed industrially may be of a type allowing continuous operation and possessing facilities for controlling the toxic methanol vapors which would be present in a methyl ester process. The relative simplicity of the ester interchange reaction may encourage some manufacturers to investigate the process, either for soap making or for other uses. The effect on vegetable and animal oil consumption and on the glycerine supply might be important if uses other than soap-making develop.

Many of the physical properties of the fatty esters suggest possibilities of extensive use. They are relatively high-boiling, are soluble in alcohol, and are compatible with a number of hydrophobic materials. It may prove possible to sell the esters at a price not much higher than that of the oil from which they are made. Their compatibility with nitrocellulose suggested some experiments which led to the tentative conclusion that they would be good plasticizers for nitrocellulose lacquer films. The esters are likewise compatible with some synthetic rubbers, and have given promise as plasticizers therefor. Other uses for high-boiling alcohol-soluble materials will undoubtedly suggest themselves to those who are interested in compounds with such a combination of properties.

The polymerization of methyl fatty esters, followed by reaction of the polymer with polyfunctional alcohols or amines by interchange, has been studied elsewhere. The products are resins with new and useful properties. This application of ester interchange and the resultant release of quantities of glycerine may become important.

One observation which may be of special interest to those in the resin field is that when furfuryl fatty esters are treated with mineral acids, resinification occurs. The reaction may be similar to that involved in the formation of cumarone-indene resins. The fatty acid groups on the products would be expected to confer valuable properties. For example, if furfuryl esters of drying oil acids were used, the resins might have possibilities of further polymerization through oxidation. This phase of the work was not thoroughly investigated.

Summary

The application of the ester interchange reaction to triglycerides has been reviewed briefly. This process gives promise of becoming commercially important, in which case substantial quantities of glycerine might be added to present sources of supply.

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Comparison of Fat-Splitting Reagents in the Twitchell Process

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The Twitchell process for the hydrolysis of fat into glycerol and fat acids has assumed increased importance because of the wartime demand for glycerol. It is a time-consuming process, however, and for that reason an improvement was sought through a study of the reaction and a comparison of the efficiency of several catalysts.

The Twitchell reagent (1) proper, made from oleic acid, sulfuric acid, and an aromatic compound, usually naphthalene, is no longer used to any extent. The petroleum sulfonic acid reagents (2), by-products in the sulfuric acid treatment of petroleum, have displaced the Twitchell reagent and reagents of a similar type.

Fat-splitting reagents in present use have certain disadvantages. The unsaponifiable matter in the reagent may contribute to unsaponifiable matter in the distilled fat acids; the dark color of the aqueous solution of the reagent contributes undesired color to the products of hydrolysis; the reagent may cause troublesome emulsions; the composition of the reagent may be variable, and in consequence the process may be somewhat unpredictable.

It would be especially desirable to have a reagent active enough to decrease considerably the time required for the approximate completion of hydrolysis and to accomplish the hydrolysis in one step without drawing off the glycerol at an intermediate stage. Our experiments have not revealed a new, fat-splitting reagent with outstanding, practical advantages, but certain observations and comparisons have been made which we consider of interest to report.

The fat-splitting reagents examined were commercial petroleum sulfonic acids, commercial wetting agents which are fat-splitting catalysts in the form of the free alkylarylsulfonic acid, Twitchell reagents, and sulfoarylstearic acids. The sulfoarylstearic acids were prepared by the Friedel and Crafts reaction between oleic acid and an aromatic compound, and

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subsequent sulfonation with sulfuric acid (3). Sulfonaphthylstearic acid has been found by Schlutius to have fat-splitting properties (4). In our work the benzenoid compounds were explored, since they can be obtained in a higher yield. Sulfoxylylstearic acid was selected from several homologs because of its greater activity and ease of preparation.

The alkylarylsulfonic acids proved to be the most effective reagents. Sulfoxylylstearic acid, seven petroleum sulfonic acids, and four Twitchell reagents followed in decreasing order.

Experimental

The fats used in comparative hydrolytic experiments were tallow, lard oil, cottonseed oil, garbage grease, and inedible grease.

Pretreatment of fats. Pretreatment of the fat is desirable in order to remove proteinaceous matter and inorganic salts, which may inactivate the catalyst. The fats were refluxed and agitated with a sulfuric acid solution at 105°C.; the aqueous layer was removed, and the fat washed free of sulfuric acid. Inedible grease and garbage grease were treated with 3 percent of sulfuric acid (based on the weight of the fat) using 20° Bé acid. Lard oil, tallow, and cottonseed oil were treated with 1 percent of 6° Bé acid. Pretreatment may not always be necessary, particularly for better grade fats. Time can be saved if this step is omitted.

Pretreatment and preparation of the fat-splitting reagents. The petroleum sulfonate reagents are frequently marketed as salts of sodium or other metals. Some of them are not very effective in this form unless they are converted to the free acid and the inorganic salts formed by metathesis are removed. All the petroleum sulfonate reagents examined were heated with thrice the stoichiometric quantity of 5 N sulfuric acid, based on the ash content of the reagent. The viscous mass formed was collected in ethyl ether, and the ether evaporated. Three of the commercial petroleum sulfonate reagents were analyzed for "soap" (active fat-splitting ingredient), oil (inert nonaqueous liquid), and volatile matter by the method of Archibald and Baldeschwieler (5). The results are given in Table I.

Commercial wetting agents of the alkylarylsulfonate type were converted from the sodium salt to the free acid by solution in water, precipitation with sulfuric acid, collection in ethyl ether, and evaporation of the ether.

Sulfoxylylstearic acid was prepared by the sulfonation of the Friedel and Crafts reaction product from commercial oleic acid and xylene, in an overall yield of 93 percent and a purity of 80 percent. Purer preparations did not have a commensurate increase in fat-splitting efficiency.

TABLE I

Analysis* of Petroleum Sulfonate Reagents

Reagent	Soap, %	Oil %	Volatile matter, %
G	52.8	37.0	10.2
D	61.3	12.3	28.0
B	82.0	10.8	7.5

*Analyses by H. B. Knight, Oil and Fat Division of this laboratory.

The Twitchell reagents were made from concentrated sulfuric acid, oleic acid, and the aromatic hydrocarbon, in the molar proportion of 8:1:1, respectively. Sulfuric acid was added gradually to the agitated mixture of oleic acid and hydrocarbon (naphthalene, xylene, benzene, or cymene). After one hour of stirring at 50° C., the mixture was poured into water and the viscous oil was collected with ethyl ether. The ether was then evaporated.

Method of hydrolysis. A 1-liter, 3-neck, round-bottom flask was charged with 100 grams of fat and 100 ml. of an aqueous solution containing the desired quantity of sulfuric acid and of the reagent. The flask was placed in a constant-temperature oil bath accommodating four flasks at one time. Each flask was equipped with a glass stirrer, a reflux condenser, and a thermometer. The flask and contents were heated to 100° C., and mechanical stirring was started. Reaction time was reckoned from the moment stirring started. At intervals, usually of four hours, the flask was withdrawn, the layers were allowed to separate, and the acid number of the nonaqueous layer was determined. After a certain degree of hydrolysis the aqueous layer was separated and replaced by 100 ml. of a sulfuric acid solution. Without further addition of the fat-splitting reagent, the experiment was continued. The percentage of hydrolysis which had taken place after any given time, t, was determined by the formula:

$$\%\ \text{Hydrolysis}_t = \frac{\text{Acid No.}_t \times 100}{\text{Acid No. of fat acid isolated by alkaline saponification.}}$$

Trials with different ratios of fat to aqueous solution showed that the speed of hydrolysis was not affected. A constant ratio of 1:1 was selected for convenience in our experiments, although in plant practice the use of a lower ratio would facilitate glycerol recovery.

Discussion of results. Comparative data on the five fats are recorded in Table II. The hydrolysis of lard oil was studied in greater detail than that of the other four fats. Reagents found most effective with one fat were most effective for all.

TABLE II

Hydrolysis of Five Fats

Conditions: Ratio of fat: water = 1:1; 1 percent alkylarylsulfonic acid reagent II; 1 percent H_2SO_4. Sweet water removed at 8 hours, as indicated by the boldface line.

Fat	Constants of original fat					Hydrolysis, %, at indicated hours			
	Unsapon. matter, %*	Sapon. No.	Acid No.	Acid No. of fat acid isolated by alkaline saponification	Hydrolysis of original fat, %	4	8	12	16
Tallow	1.31	205.0	41.9	195.8	21.4	81.0	94.1	99.4	......
Lard oil	1.21	194.1	5.2	198.0	2.6	74.2	90.6	98.3	......
Cottonseed oil	......	194.8	0.6	198.0**	0.3	68.9	91.3	98.0	......
Garbage grease	3.16	188.5	16.1	194.5	8.3	76.4	92.3	97.1	98.8
Inedible grease	......	192.2	54.6	195.2	28.1	78.9	89.7	95.7	97.1

*Determined by a simplified continuous petroleum-ether extraction method (7). **Assumed.

TABLE III

Various Fat-Splitting Reagents in the Hydrolysis of Lard Oil

Conditions: 1 percent H_2SO_4 solution, ratio of fat: water = 1:1. Sweet water removed at 8 hours in experiments 2 to 5, inclusive, and at 12 hours in experiments 6 to 13, inclusive, as indicated by the boldface line.

Expt.	Reagent	Reagent, %	Hydrolysis, %, at indicated hours					
			4	8	12	16	20	24
1	No reagent	0	2.7	3.2	3.5	......	......	......
2	Alkylarylsulfonic acid I	1	67.3	90.4	98.4	......	......	......
3	Alkylarylsulfonic acid II	1	74.2	90.6	98.3	......	......	......
4	Alkylarylsulfonic acid II	¾	71.2	90.9	97.4	......	......	......
5	Alkylarylsulfonic acid II	½	56.8	84.6	91.0	96.6	......	......
6	Sulfoxylylstearic acid	1	65.0	88.8	92.6	98.3	......	......
7	Petroleum sulfonic acid A	1	65.3	86.4	91.4	96.8	98.4	98.2
8	Petroleum sulfonic acid B	1	64.3	87.8	91.4	96.8	97.4	96.9
9	Petroleum sulfonic acid C	1	61.4	85.9	90.4	96.1	97.6	98.1
10	Petroleum sulfonic acid D	1	71.1	90.2	91.9	95.4	95.9	97.2
11	Petroleum sulfonic acid E	1	32.4	72.9	86.2	93.8	96.3	97.2
12	Petroleum sulfonic acid F	1	31.6	72.0	85.8	92.8	95.9	97.1
13	Petroleum sulfonic acid G	1	33.9	65.2	80.8	89.1	93.5	96.2
14	Twitchell: naphthalene	1	19.7	70.4	......	......	......	......
15	Twitchell: xylene	1	21.1	67.7	......	......	......	......
16	Twitchell: benzene	1	20.1	64.2	......	......	......	......
17	Twitchell: cymene	1	11.5	37.9	......	......	......	......

Hydrolysis of lard oil. Comparative data on fourteen reagents are given in Table III. The reagents are listed in the order of their effectiveness. Because of their greater activity, the alkylarylsulfonic acid reagents may be used in a concentration less than 1 percent. Sulfoxylylstearic acid is only slightly superior to the better petroleum sulfonic acid reagents. The Twitchell reagents appear to be approximately equal to the least effective petroleum sulfonic acid reagents. Untabulated experiments showed that the use of a reagent concentration greater than 1 percent had no proportional advantage.

In order to reach approximate completion of hydrolysis, the sweet water must usually be replaced by a sulfuric acid solution and the reaction continued. The time at which this change is effected has an important influence on the speed of hydrolysis. In the experiments recorded in Table IV, in which 1 percent sulfoxylylstearic acid was used as the reagent, the optimum time is when hydrolysis is 85 percent completed. If the change is made very much earlier or later, the time required for the approximate completion of hydrolysis is increased. This is true also of the petroleum sulfonic acid reagents.

Selection of the best time at which to remove the sweet water is complicated by the problem of glycerol recovery. It may be desirable to remove the sweet water when the hydrolysis is greater than 85 percent in order to obtain a greater concentration of glycerol, particularly when the original fat is partly hydrolyzed. It may also be desirable in replacing the sweet water to use the dilute sweet water from a previous run or in certain cases even to start the reaction with a dilute sweet water.

Table IV also illustrates that sulfuric acid must be present, but that one-half of 1 percent is nearly as effective as 1 percent.

Distribution of fat-splitting reagents between phases. The practice of replacing the sweet water by a sulfuric acid solution and continuing the hydrolysis indicates that sufficient reagent exists in the nonaqueous phase to enable the reaction to proceed. The sulfoxylylstearic acid reagent is sparingly soluble in the original triglyceride but becomes increasingly soluble in the nonaqueous phase as the glyceride content decreases and the fat acid content increases.

The distribution of the reagent between phases during hydrolysis could not be determined by titration of aqueous and nonaqueous layers. The total acidity was greater than could be accounted for by the sulfuric acid, reagent, and known degree of hydrolysis. It was found, however, that sulfoxylylstearic acid could be nearly quantitatively precipitated from an aqueous solution by S-benzylthiuronium chloride, and this furnished a method for determining the distribution of the reagent. Mixtures of lard oil and an aqueous solution of sulfuric acid and the reagent as used in the fat-splitting tests were investigated. Under conditions representing different stages in the hydrolysis, the aqueous layer was carefully separated and neutralized with sodium hydroxide, and the reagent was precipitated in the cold with an aqueous solution of S-benzylthiuronium chloride (6). The precipitate was collected at 5° to 10° C. on a funnel having a fritted glass disc and dried to constant weight in a vacuum desiccator. Weight of precipitate × 100 ÷ weight of precipitate obtained from the original aqueous solution containing 1 percent sulfoxylylstearic acid and 1 percent sulfuric acid = percent of sulfoxylylstearic acid in the aqueous phase.

The results are represented in Figure 1, from which it is apparent that increasing hydrolysis is associated with an increasing proportion of the reagent in the

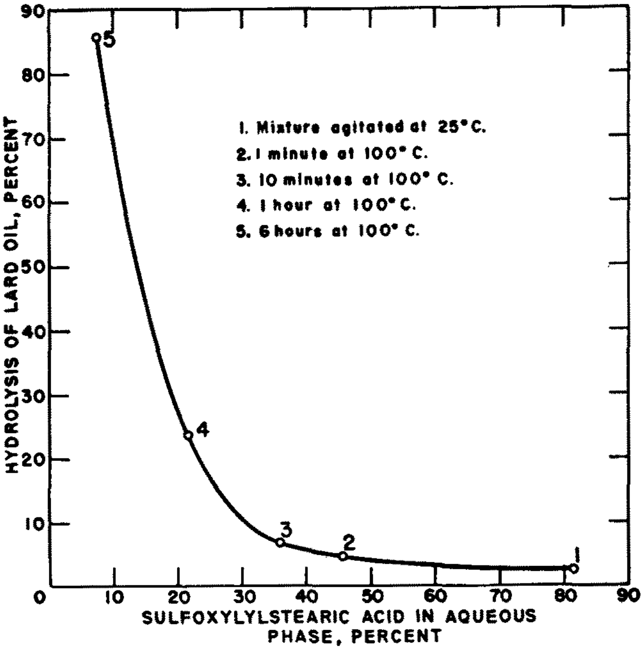
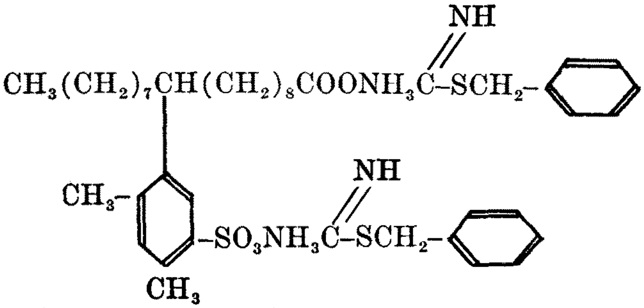


Fig I, Distribution of Fat-Splitting Reagent between Phases nonaqueous phase. This method applied to other reagents might help to explain how the catalyzed hydrolysis takes place and why some reagents are better than others.

After precipitation from dioxane solution by the addition of water and subsequent drying by extraction with petroleum ether, the product from S-benzylthiuronium chloride and sulfoxylylstearic acid had a m.p. of 98° to 99.5° C. When analyzed* it gave the following results:

Calculated for $C_{34}H_{54}O_5N_2S_2$: % N, 4.41; % S, 10.10
Calculated for $C_{42}H_{64}O_5N_4S_3$: % N, 7.00; % S, 12.00
Found : % N, 6.90; % S, 10.59.

The analysis suggests that the product consists largely of a compound $C_{42}H_{64}O_5N_4S_3$ having a formula such as



Color of fat acids in the Twitchell process. The dark color of the fat acids formed in the Twitchell process makes them unsuitable for many purposes, and distillation is required. The dark color appears to depend on the time of exposure of the unsaturated fat acids to oxidation at about 100° C. The fat-splitting reagent contributes to color if the reaction time must be prolonged to reach a sufficient degree of hydrolysis or if it is black and impure and directly contributes color. The organic sulfonic acid reagent present in the same phase with the fat acids may react with the fat acids, causing discoloration.

In Table V are presented some results showing the effect of some fat-splitting reagents upon the color of crude fat acids produced in the hydrolysis of lard oil. The petroleum sulfonic acid reagents B and D produced fat acids lighter in color at approximately the same degree of hydrolysis effected by the alkylarylsulfonic acid reagent II and sulfoxylylstearic acid. The darkest reagent, petroleum sulfonic acid reagent G, was the least effective and produced the darkest fat acids. However, when the crude fat acids were distilled, the color was about the same, regardless of the reagent used. The acids distilled at 165° to 175° C. at 0.5 mm. The color, measured in the Lovibond tintometer, using a 1-inch cell, was 2.5 yellow, 0.3 red.

TABLE V

Color of the Crude Fat Acids Produced in the Hydrolysis of Lard Oil

Conditions: Open steam; free flame; air condenser; all-glass apparatus; fat: water ratio = 1:1; 1 percent H_2SO_4; 1 percent reagent. Sweet water removed at 80-percent completion.

Expt.	Reagent	Hydrolysis		Color of fat acid (Lovibond; 5-mm. cell)	
		Hours	%	Yellow	Red
1	Petroleum sulfonic acid D	16	95.1	30.0	4.1
2	Petroleum sulfonic acid B	16	97.7	30.0	6.3
3	Alkylarylsulfonic acid II	12	97.2	30.0	9.3
4	Sulfoxylylstearic acid	16	98.8	30.0	9.6
5	Petroleum sulfonic acid G	28	86.2	30.0	10.3

Summary

Commercial petroleum sulfonic acid reagents have been compared with Twitchell reagents, alkylarylsulfonic acids, and sulfoarylstearic acids as fat-splitting reagents in the hydrolysis of lard oil, tallow, cottonseed oil, garbage grease, and inedible grease. The best reagents were made from commercial wetting agents of the alkylarylsulfonate type. Sulfoxylylstearic acid, seven petroleum sulfonic acids, and four Twitchell reagents followed in decreasing order.

Observations have been made on the distribution of the fat-splitting reagent between phases, the necessity of removing the sweet water after a certain degree of hydrolysis, and the effect of the fat-splitting reagent upon the color of the crude fat acids.

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TABLE IV

Effect of Time of Removal of Sweet Water and Effect of Sulfuric Acid in the Hydrolysis of Lard Oil

Conditions: Ratio of fat: water = 1:1; reagent = 1 percent sulfoxylylstearic acid. Sweet water removed and replaced by a sulfuric acid solution at the time indicated by the boldface line.

Expt.	H_2SO_4, %	Hydrolysis, %, at indicated hours						
		4	6	8	10	12	16	20
1	1	65.0		88.8		92.6	92.8	97.1
2	1	65.0		88.8		92.6	98.3	......
3	1	65.0		88.8		97.0	98.8	......
4	1	65.0	85.5		96.0	98.4	......	......
5	1	65.0		90.4		95.6	97.4	......
6	½	66.8	83.2		94.6	97.6	......	......
7	0	22.5		66.9		85.4	92.6	94.7

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*Analysis made by the Analytical and Physical Chemistry Division of this laboratory.