Results obtained by another group of Laboratories on the same sample:

Laboratory	Stability Test
8	33 hrs.
9	24 hrs.
10	34 hrs.
11	24 hrs.
12	24 hrs.
13	28 hrs.
14	30 hrs.
15	34 hrs.
16	28 hrs.
17	32 hrs.
18	30 hrs.
19	30 hrs.
20	30 hrs.
21	28 hrs.
22	33 hrs.
23	29 hrs.
Average	29 hrs.

Results obtained by an Independent Laboratory: 12 hrs.

The foregoing results were obtained by using the method as it was originally published by King, Roschen, and Irwin in *Oil and Soap, 10,* 105 (1933). Further work is necessary and will be carried on during the next year.

Other Methods

Work on methods other than those mentioned above is on our program but there is no progress to report at this time.

L. B. PARSONS
J. FITELSON
C. P. LONG
K. S. MARKLEY
H. A. SCHUETTE
J. E. MARONEY
E. W. BLANK
E. W. COLT
L. M. TOLMAN
M. L. LAING
F. C. WOEKEL
S. O. SORENSEN
V. C. MEHLENBACHER, *Chairman*

A Report on Ester Interchange

H. J. WRIGHT, J. B. SEGUR, H. V. CLARK, S. K. COBURN, E. E. LANGDON and R. N. DuPUIS

Glycerine Producers' Association Research Laboratories

Ester interchange may be defined broadly as a reaction between an ester and an alcohol. Another name for this effect is alcoholysis, meaning a decomposition involving alcohol. A typical example is the reaction between methanol and a triglyceride to give glycerine and methyl fatty acid esters. Another example well known to the industry is the treatment of triglycerides with glycerine to give mono- and di-glycerides. Alkaline catalysts are ordinarily used, although in some cases acids are preferred.

Ester interchange between glycerides or other fatty acid esters and various alcohols has been the subject of research by this laboratory. Types of ester interchange reactions of these materials to be dealt with here include reactions of monohydric alcohols with esters of polyhydric alcohols, monohydric alcohols with esters of monohydric alcohols, polyhydric alcohols with esters of polyhydric alcohols and polyhydric alcohols with esters of monohydric alcohols.

Ester interchange between monohydric alcohols and glycerides can be effected in the presence of small amounts of alkalies or acids. The glyceride is thereby converted almost entirely into free glycerine and fatty acid esters of the monohydric alcohol used. The lower alcohols, methyl and ethyl, react rapidly and smoothly with glycerides in the presence of sodium hydroxide (2, 7). A typical reaction would require 1.6 equivalents of anhydrous methyl or ethyl alcohol per equivalent of a neutral glyceride with 0.5% sodium hydroxide, on the basis of the oil, as catalyst, dissolved in the alcohol. The alcoholic sodium hydroxide solution is merely mixed with the glyceride until homogeneous. This reaction may be carried out at room temperature or at higher temperatures, if necessary to keep the glyceride more fluid. Within thirty minutes glycerine starts to separate as a lower layer and in from one to two hours has separated almost completely. The glycerine layer is withdrawn, the ester layer acidified to break up any soap formed and washed free of unsettled glycerine, unreacted alcohol and salt.

For best results, the materials used should meet certain qualifications. When ethyl alcohol is used and the acid number of the glyceride is below about one, the reaction takes place as described previously. If the acid number is somewhat greater than this it may be at least partly compensated by adding sodium hydroxide in excess of catalytic amounts to neutralize free acids. However, because of the resulting soap formation the reaction mixture tends to become viscous or to gel. The reaction mixture must then be acidified after a standing period to permit separation of the alcohol-glycerine and the fatty acid-ester layers. Gels or viscous reaction mixtures may sometimes be prevented by using a larger excess of alcohol, but in these cases the glycerine will be held in solution. Acidification of the reaction mixture is necessary here also to promote separation of layers.

Another prerequisite for effectively carrying out the reaction is that the materials be substantially anhydrous. Presence of water causes soap formation, with consequent loss of alkalinity. For example, when 30 parts ethyl alcohol, 0.5 part sodium hydroxide and 100 parts cottonseed oil are used, as little as 0.3% water in the reaction mixture appreciably lowers the glycerine yield and causes the reaction mixture to become viscous, preventing separation of glycerine. Sodium hydroxide in excess of catalytic amounts and/or excess alcohol may be used to compensate in some measure for the presence of water. In these cases the reaction mixtures usually must be acidified to cause separation of the glycerine and ester layers. The specific effects of water on the reaction using cottonseed oil with ethyl alcohol are given in Table I.

TABLE I

Effects of Water on Ester Interchange Reactions
Using 100 g. anhydrous cottonseed oil with ethyl alcohol

Ethyl alcohol (99.5% by wt.) (g.)	Water in alcohol (g.)	Amount of added water (g.)	Total amt. of water in batch (g.)	NaOH used (g.)	Per cent water in batch	Per cent glycerine yield
30	0.15	0.0	0.15	0.5	0.11	89.4
30	0.15	0.15	0.30	0.5	0.23	88.0
30	0.15	0.3	0.45	0.5	0.34	79.5
30	0.15	0.6	0.75	0.5	0.57	61.8
30	0.15	0.0	0.15	1.0	0.11	96.6
30	0.15	0.3	0.45	1.0	0.34	90.2
30	0.15	0.6	0.75	1.0	0.57	90.2
30	0.15	0.9	1.05	1.0	0.80	82.8
40	0.2	0.0	0.2	0.5	0.14	87.9
40	0.2	0.2	0.4	0.5	0.28	87.3
40	0.2	0.4	0.6	0.5	0.43	86.4
40	0.2	0.8	1.0	0.5	0.71	65.8
40	0.2	0.0	0.2	1.0	0.14	93.5
40	0.2	0.2	0.4	1.0	0.28	91.7
40	0.2	0.4	0.6	1.0	0.42	93.5
40	0.2	0.8	1.0	1.0	0.79	90.7

Similar results are shown in Table II using coconut oil with ethyl alcohol. In these experiments lower yields were obtained using the same weight ratios of reactants as in the cottonseed oil runs because coconut oil has the lower molecular weight and therefore requires more alcohol per gram of oil.

Normal propyl alcohol is less reactive than ethanol or methanol, but good yields may be obtained by using larger excesses of propyl alcohol. Here the reaction mixture must always be acidified to effect separation of the glycerine layer. Amounts of reactants necessary to obtain satisfactory yields with normal propyl alcohol are given in Table III.

Isopropyl alcohol was tried, but appeared to be impractical from a commercial standpoint because the reaction mixture must be free of all moisture and metallic sodium must be used in order to produce active catalysis of the reaction.

Other alcohols which have been used in this type of reaction include: furfuryl alcohol, methyl, ethyl and benzyl "Cellosolves." In most of these cases large excesses of alcohol must be used for even fairly complete reaction. Usually glycerine does not separate from the reaction mixture. Other methods of preparing these esters, to be described, are probably more advantageous in these cases.

A step-wise addition of the alcohol and removal of glycerine has been reported (2) to be advantageous in that less alcohol may be used in the reaction. This has been confirmed in our laboratory in the case of methanol, but when addition of ethyl alcohol is attempted in this manner the reaction tends to gel.

A continuous method of producing methyl esters from glycerides has been tried in this laboratory. In these experiments the glyceride, methyl alcohol and caustic were mixed at 65° C. and held for five minutes at this temperature. This reaction mixture was then run through a Sharples laboratory centrifuge. It was estimated that a yield of 85% of the theoretical amount of glycerine could be obtained in this manner with a through-put of 100 to 500 gallons an hour. More precise information is lacking because the centrifuge was small and had no facilities for temperature control. Higher temperatures in this case reduced the viscosity of the reaction mixtures and facilitated the removal of glycerine.

TABLE III

Reaction Conditions for Ester Interchange with Glycerides and n-Propyl Alcohol
(All reactions run at room temperature)

Oil 100 g.	n-propyl alcohol (g.)	Per cent of theory for alcohol	NaOH (g.)	Glycerine yields (%)
Cottonseed	100	476	5.0	85.1
Cottonseed	100	476	3.0	87.9
Peanut	100	498	0.5	88.7
Peanut	100	498	0.2	72.9
Peanut	75	373	1.0	94.2
Peanut	50	249	3.0	96.6
Peanut	50	249	2.0	96.9
Peanut	50	249	1.0	85.4
Peanut	50	249	0.5	72.8
Peanut	40	199	3.0	97.2
Peanut	40	199	2.0	98.5
Peanut	40	199	1.0	88.1
Peanut	30	149	2.0	84.0
Cottonseed	25	119	1.0	36.9
Cottonseed	25	119	0.1	0.0

Acid catalysis has also been used to effect this type of reaction (3, 6). The acid-catalyzed reaction has been only superficially investigated in this laboratory, but seems to offer less satisfactory possibilities than the alkali-catalyzed reaction for large excesses of alcohol must be used to obtain an advantageous equilibrium and spontaneous separation of glycerine is not obtained.

Ester interchange was carried out between methyl esters of fatty acids and various other monohydric alcohols. Methyl esters of fatty acids were heated at 200° C. with furfuryl alcohol in the presence of catalysts such as litharge, lead naphthenate, lead soaps, and various alkaline salts. The evolved methanol was allowed to distil from the reaction, while the furfuryl alcohol was condensed and returned. The amount of catalyst used to carry out the reaction was from 0.3 to 0.5% of the total reaction weight. Other alcohols which were esterified in this manner

TABLE II

Effects of Water on Ester Interchange Reactions
Using 100 g. coconut oil with ethyl alcohol

Water in oil (g.)	Ethyl alcohol (99.5% by weight) (g.)	Water in alcohol (g.)	Amount of added water (g.)	Total amount of water in batch (g.)	NaOH used (g.)	Per cent water in batch	Per cent glycerine yield
0.21	30	0.15	0.0	0.36	0.5	0.28	55.4
0.21	30	0.15	0.15	0.51	0.5	0.39	40.3
0.21	30	0.15	0.3	0.66	0.5	0.50	33.9
0.21	30	0.15	0.6	0.96	0.5	0.73	17.6
0.0	30	0.15	0.0	0.15	1.0	0.11	88.2
0.21	30	0.15	0.0	0.36	1.0	0.27	91.9
0.21	30	0.15	0.3	0.66	1.0	0.5	54.1
0.0	40	0.2	0.0	0.2	1.0	0.14	94.0
0.21	40	0.2	0.0	0.41	1.0	0.29	91.9
0.21	40	0.2	0.4	0.81	1.0	0.57	83.9
0.0	30	0.15	0.0	0.15	2.0	0.11	95.4
0.21	30	0.15	0.0	0.36	2.0	0.27	92.8
0.21	30	0.15	0.3	0.66	2.0	0.5	73.2

were benzyl and methyl "Cellosolves" and tetrahydrofurfuryl alcohol.

Polyhydric alcohols were also used in place of monohydric alcohols for the interchange reactions with glycerides (1, 4, 5). The polyhydric alcohol to be substituted in this manner for the glycerine in a glyceride should be stable at reaction temperatures of 200 to 300° C. and have a boiling point higher than that of glycerine, so that glycerine may be removed during the reaction. A few materials suitable for this reaction are pentaerythritol, methyl and ethyl glucosides, mannitol, sorbitol and polyglycerols. A typical reaction comprised heating one equivalent of glyceride with 1 to 1.5 equivalents of the polyhydric material in the presence of 0.5 to 2.0 per cent of a catalyst, lead or alkaline salts as mentioned before. Lead salts are preferred as catalysts if end use of the product will permit, for the lead salts can be more easily removed from the reaction product than the soaps formed by alkaline catalysts. If the reaction is run at atmospheric pressure the temperature employed should be around 275-300° C., i.e., high enough to drive off the glycerine. However, if vacuum is employed the reaction may be carried out at 200 to 250° C., at which temperatures glycerine will distil at pressures of 40 to 300 mm. Pressures lower than these are preferred, however. In cases where unsaturated glycerides are used and the reaction mixture bodies somewhat, it has been found advantageous to employ a steam-vacuum distillation when the catalyst is a lead salt, and a toluene, carbon tetrachloride or other suitable organic solvent vacuum distillation, to inhibit foaming, when an alkaline catalyst is used. These distillations greatly facilitate the removal of glycerine.

This type of reaction was carried out on a continuous basis by heating the reactants until homogeneous and then slowly running the reaction mixture into the top of a long, heated glass column. The system was evacuated through a side arm and receiver near the top of the column. As the reaction mixture trickled over the heated sides of the column, glycerine was released and was collected at the side arm receiver while the reaction product was collected at the bottom of the tube. Several passes were necessary for complete reaction.

Ester interchange was carried out successfully between polyhydric alcohols and fatty acid esters of monohydric alcohols. If methyl esters of fatty acids are heated at 200 to 300° C. with a polyhydric alcohol in the presence of catalysts such as lead salts or alkaline salts, methyl alcohol will distil from the reaction mixture and esters of the polyhydric alcohol will be formed. Conditions are given in Table IV for reactions between pentaerythritol and linseed methyl esters. Such a reaction will start at about 175° C., but higher temperatures are necessary to secure reasonably complete reaction as indicated by low hydroxyl values. In the case of polyhydric materials which distil at reaction temperatures a hot condenser may be used which will allow methanol to distil but will reflux the polyhydric material. The reaction is held at the lower temperatures in these cases until the polyhydric alcohol has partially reacted, in order to prevent excessive reflux and flooding of the condenser. Then the temperature is raised and the reaction brought to completion. Polyhydric materials which were esterified in this manner include glycols, pentaerythritol, mannitol, polyglycerine and methyl and ethyl glucosides.

TABLE IV

Reaction of Pentaerythritol with Methyl Esters of Linseed Oil Acids

(100 g. methyl esters of linseed oil used in all runs)

Pentaerythritol (g.)	Per cent Pb added as naphthenate	Treatment	Acid No. of product	Hydroxyl No. corrected for acid No.
11.0 (90% theory)	1	4 hrs. at 225°C.	6.02	36.32
9.8 (80% theory)	1	4 hrs. at 225°C.	4.57	27.57
8.58 (70% theory)	1	4 hrs. at 225°C.	4.06	23.36
11.0 (90% theory)	1	8 hrs. at 225°C.	5.19	31.69
12.26 (theory)	1	2 hrs. at 280°C.	12.52	16.99
12.26 (theory)	1	2 hrs. at 225°C. plus 2 hrs. at 280°C.	7.88	21.48
12.26 (theory)	1	1 hr. at 280°C.	6.82	22.82
12.26 (theory)	0.5	2 hrs. at 280°C.	7.23	16.33

Although some of the above described reactions have been carried out in industry, applications have not been numerous. The possibilities of future utilization of these reactions may be evaluated by listing some advantages and disadvantages of ester interchange processes as compared with present practices. Some possible end uses of products of ester interchange reactions will be indicated.

When ester interchange is used to split fats and form methyl or ethyl esters of the fat acids, the reaction proceeds rapidly and glycerine separates in a fairly concentrated alcoholic solution which can easily be removed and further concentrated. Much color is removed in this glycerine layer and the ester layer, after one or two washes, will be usable in many cases without further treatment and will give an exceptionally light-colored product with one distillation. These esters of fatty acids can be distilled and fractionated at lower temperatures than fatty acids. Alkali, Twitchell or autoclave methods of fat splitting are slower and tie up equipment for a longer time. In the case of alkali saponification, the soap is acidified to recover the fatty acids and glycerine is obtained in a dilute solution together with much salt. Fatty acids produced by the Twitchell process are dark in color and in many cases have to be distilled before use.

Perhaps the principal disadvantage in the ester interchange process of fat splitting is the necessity for working with a refined, anhydrous oil for best results. All reactants and apparatus must be dried before use for maximum efficiency. In addition, the cost of the alcohol must be taken into account. This should include recovery and makeup costs. The simplest alcohol to use is methanol, since it gives a good yield, is readily obtainable in the anhydrous form and is easy to recover. It has the disadvantage of toxicity. When a nontoxic process or product is required, ethyl alcohol is ordinarily used, but its use involves considerations of government distillation permits and special dehydrating equipment for the recovered alcohol. On a large-scale operation, these disadvantages may be offset by the simplicity and speed of the process.

Esters of higher molecular weight can be produced from the monohydric alkyl esters by ester interchange about as readily as by direct esterification of fatty acids with alcohols. In many cases the esters produced by interchange are lighter in color than those made by direct esterification. In special cases, such 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.

BIBLIOGRAPHY

1. Blangonrovova, A. A., and Antipova, M. A. Byull. Obmen Opyt. Lakokrasochnoi Prom. *1940*. No. 10, 18-19.
2. Bradshaw, G. B., and Meuly, W. C. (to E. I. du Pont de Nemours & Co.). U. S. Patent 2,271,619 (Feb. 3, 1942).
3. Coleman, G. H., and Moore, G. V. (to Dow Chemical Co.). U. S. Patent 2,010,689 (Aug. 6, 1935).
4. Irvine, J. C., and Gilchrist, H. S. J. Chem. Soc. *125*, 1-10 (1924).
5. Lapworth, A., and Pearson, L. K. Biochem. J. *13*, 296-300 (1919).
6. Madinaveitia, A. Madrid Anes. soc. espan. fis. quim. *12*, 426-8 (1914).
7. Tsuchiya, T., and Ishikawa, T. J. Soc. Chem. Ind. Japan *36*, Suppl. Binding 230-3 (1933); Chem. Abs. *27*, 3630.

Comparison of Fat-Splitting Reagents in the Twitchell Process

A. J. STIRTON, E. M. HAMMAKER, S. F. HERB, and EDWARD T. ROE
Eastern Regional Research Laboratory[1]
Philadelphia, Pennsylvania

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

---

[1] This is one of four Regional Research Laboratories operated by the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.