retical principles of liquid thermal diffusion have not been fully developed. Factors which affect the degree of separation in the thermal diffusion process are uniformity of size of the annular space, temperature differential, and time required for diffusion. It appears that this method may be adapted for continuous operation.

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Ester Reactions of Fatty Materials[1]

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REACTIONS involving ester linkages of fats and oils are among the most important in the chemistry of fatty acid derivatives. Hydrolysis of esters under alkaline conditions, the familiar saponification of fats and oils, has been practiced for centuries. This paper will cover the nonhydrolytic ester reactions: esterification, alcoholysis, acidolysis, and interesterification. These reactions are of far more recent origin and have been recognized for approximately one century. However it has only been within the past few decades that they have assumed technical importance. Alkyd resins, rubber-like polyesters, improved lard for shortening, and nonionic surface active agents, to improve shortening efficiency and soften bread, represent only a few of the products dependent upon these ester reactions.

M. W. Formo

General Scope and Chemistry of the Ester Reactions

There are four closely allied reversible reactions involving addition or interchange of alkyl radicals on the carboxyl residue of fatty acids. These reactions, which have much in common, are as follows:

1. Esterification is the condensation of an acid and an alcohol to give an ester and water; the reverse reaction is hydrolysis.

$$RCOOH + R'OH \rightleftharpoons RCOOR' + HOH$$

2. Alcoholysis involves the replacement of the alkyl group of an ester by another through interaction of the ester and an alcohol. The reaction is frequently described in terms of the added alcohol, e.g. methanolysis, glycerolysis, etc.

$$RCOOR' + R''OH \rightleftharpoons RCOOR'' + R'OH$$

3. Acidolysis, in an analogous way, is the substitution or exchange of acyl groups of esters through the reaction of an ester and an acid.

$$RCOOR' + R''COOH \rightleftharpoons R''COOR' + RCOOH$$

4. Interesterification, sometimes termed ester interchange or trans-esterification, is the exchange of acyl and alkyl groups between a pair of esters.

$$RCOOR' + R''COOR''' \rightleftharpoons RCOOR''' + R''COOR'$$

There has been some confusion in the literature regarding the nomenclature of these related reactions. Some authors use the terminology, "trans-esterification reactions," broadly to describe alcoholysis, acidolysis, and interesterification. Others use the term "interesterification reactions" in a similar broad sense (German "Umesterung"). It is becoming more common practice to use the term "trans-esterification" as a synonym for interesterification or ester-interchange to describe the exchange of acyl and alkyl groups between a pair of esters. Such terminology will be adhered to in this discussion.

The close relationship between esterification, alcoholysis, and interesterification is illustrated by comparison of the equilibrium constants for homogeneous reaction. Normally we do not have sufficient data to calculate all equilibrium constants, but theoretically the point of equilibrium in both alcoholysis and interesterification reactions can be calculated from the simple esterification constants.

Study of esterification and hydrolysis provided some of the earliest classical examples of reversible equilibria. At equilibrium in a homogeneous reaction the relationship between concentrations of reactants and products is represented by the familiar esterification constant.

$$\text{Acid} + \text{Alcohol} \rightleftharpoons \text{Ester} + \text{Water}$$

$$\frac{[\text{Ester}] \times [\text{Water}]}{[\text{Acid}] \times [\text{Alcohol}]} = \text{K esterification}$$

Table I illustrates the relationship of the esterification equilibrium constant to the alcoholysis and interesterification equilibria. Knowledge of esterification constants would permit calculation of the equilibria in both alcoholysis and interesterification reactions.

Several reviews are available covering the ester reactions (1, 2, 3, 4, 5).

Esterification Reactions

There are four primary methods for direct preparation of esters:

1. reaction of an alcohol and an acid with elimination of water;

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[1] Technical Paper No. 130 from the Archer-Daniels-Midland Company.

TABLE I

EQUILIBRIUM CONSTANTS IN ESTERIFICATION ALCOHOLYSIS AND INTERESTERIFICATION REACTIONS

ESTERIFICATION REACTION:

REACTION OF ACID, RCOOH, WITH ALCOHOLS R^2OH AND R^3OH

$$RCOOH + R^2OH \rightleftharpoons RCOOR^2 + H_2O$$

$$K_1 = \frac{(RCOOR^2)\ (H_2O)}{(RCOOH)\ (R^2OH)}$$

$$RCOOH + R^3OH \rightleftharpoons RCOOR^3 + H_2O$$

$$K_2 = \frac{(RCOOR^3)\ (H_2O)}{(RCOOH)\ (R^3OH)}$$

SIMILARLY FOR ACID, R'COOH, WITH ALCOHOLS, R^2OH AND R^3OH

$$K_3 = \frac{(R'COOR^2)\ (H_2O)}{(R'COOH)\ (R^2OH)}; \qquad K_4 = \frac{(R'COOR^3)\ (H_2O)}{(R'COOH)\ (R^3OH)}$$

ALCOHOLYSIS REACTION:

$$RCOOR^2 + R^3OH \rightleftharpoons RCOOR^3 + R^2OH$$

$$KAL\text{-}1 = \frac{(RCOOR^3)\ (R^2OH)}{(RCOOR^2)\ (R^3OH)} = \frac{K_2}{K_1}$$

$$R'COOR^2 + R^3OH \rightleftharpoons R'COOR^3 + R^2OH$$

$$KAL\text{-}2 = \frac{(R'COOR^3)\ (R^2OH)}{(R'COOR^2)\ (R^3OH)} = \frac{K_4}{K_3}$$

INTERESTERIFICATION REACTION:

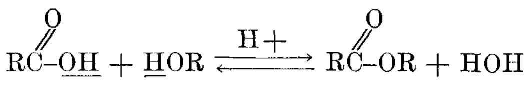
$$RCOOR^2 + R'COOR^3 \rightleftharpoons RCOOR^3 + R'COOR^2$$

$$K\text{-}INTERESTERIFICATION = \frac{(R'COOR^2)\ (RCOOR^3)}{(RCOOR^2)\ (R'COOR^3)} = \frac{KAL\text{-}1}{KAL\text{-}2} = \frac{K_2}{K_1}\ \frac{K_3}{K_4}$$

2. reaction of an alcohol and an acid anhydride to form an ester and an acid;
3. reaction of an alcohol and an acid chloride with elimination of HCl;
4. reaction of an alkyl halide and a metal salt of an organic acid with elimination of the metal halide.

Indirect methods for ester formation involving alcoholysis, interesterification, and acidolysis will be considered later. Of the direct methods the only process of technical importance involves direct formation of the ester from alcohol and acid.

Esterification of carboxylic acids involves loss of water between the hydroxyl group of the acid and the hydrogen of the alcohol.



$$R\overset{O}{\overset{/\!/}{C}}\text{-}\underline{OH} + \underline{H}OR \xrightleftharpoons{H+} R\overset{O}{\overset{/\!/}{C}}\text{-}OR + HOH$$

The rate of reaction is proportional to the hydrogen ion concentration over lower ranges of acid catalyst concentration. Strong acids such as H_2SO_4, HCl, H_3PO_4, toluene sulfonic acid, Twitchell acids, etc., catalyze esterification. The reaction is bimolecular, but if a large excess of either acid or alcohol is used, the reaction is pseudo-first-order. Modern electronic concepts of the reaction mechanism are discussed by Alexander (6) and Remick (7).

Esterification of Fatty Acids with Low Molecular Weight Monohydric Alcohols. The esterification of fatty acids with lower molecular weight monohydric alcohols is normally carried out, using a large excess of the alcohol in the presence of an acid catalyst. For preparation of methyl and ethyl esters, fatty acids are commonly refluxed for several hours with from two to four times their weight of alcohol in the presence of 1% to 3% of sulfuric acid or dry hydrogen chloride. Using such large excesses of methyl alcohol (15 to 35 moles per mole of fatty acid), ester yields of 95% or higher are obtained.

The equilibrium and velocity constants of esterification of fatty acids with methyl, ethyl, and other monohydric alcohols have been the subject of classical investigations (8, 9, 10, 11). Sudborough (11) and his co-workers demonstrated that the velocity of esterification of various fatty acids from butyric to stearic was practically constant. The rate for unsaturated acids such as oleic, elaidic, erucic, and brassidic were similar and somewhat less than half that of the saturated acids. It is interesting that the esterification rates of the cis- and trans-isomers are virtually identical.

Analysis of fats for component acids usually involves fractionation of esters. The fat sample is converted to methyl esters by alcoholysis, or alternatively the sample is saponified, extracted with solvents to remove unsaponifiable constituents, acidified, and esterified with methyl or sometimes ethyl alcohol. For analytical work it has been suggested that methyl esters be formed by reaction of soaps with an excess of dimethyl sulfate in the presence of potassium carbonate (12). This reaction is convenient and quantitative. Vacuum-distillation is used to separate the methyl esters into fractions of varying boiling points and molecular size. Such determinations as refractive index, iodine value, and saponification value are used to characterize the fraction and permit calculation of the fatty acid composition. Longenecker (13) and Hilditch (14) have reviewed the literature on ester fractionation as an analytical tool. The quality of the still and the technique of operation are of major importance in application of ester fractionation for determination of fat composition (15, 16).

Fatty acids esterify far more rapidly than rosin acids with low molecular weight alcohols such as methyl, ethyl, propyl, and butyl. This difference is the basis for the analytical determination of fatty acids and rosin acids in tall oil. The mixed tall oil fatty acids are refluxed with methyl alcohol containing dry hydrogen chloride gas. The fatty acids esterify whereas rosin acids are virtually unesterified. Differences in A. V. before and after esterification permits calculation of both the fatty acids and the rosin acids (17, 18, 19). This difference in ease of esterification has been suggested as a basis for separation. Gloyer esterified tall oil and fractionated, using a combination of a non-polar solvent, such as petroleum naphtha, which preferentially dissolves the fatty esters and furfural, which is more polar and dissolves the rosin acids (20). Rosin acids can be esterified with methanol under drastic conditions by autoclaving an excess of an alcohol with rosin acids at temperatures of 280-290° C. and pressures of approximately 1,000 lbs./sq. in. (21, 22, 23).

Because the esterification is an equilibrium reaction, it can be driven to conclusion by removal of the water of reaction. In the esterification of lower alcohols, removal of water is difficult because of the closeness of boiling point of water and the lower alcohols. Azeotropic procedures likewise are not applicable because of the mutual solubility of alcohol-rich water-alcohol mixtures with normal azeotroping solvents.

Cation exchange resins of the phenol-formaldehyde sulfonic acid type have been used to catalyze esterification of oleic acid by n-butyl alcohol but offer no advantage over conventional acid catalysts (24).

Methyl and n-butyl esters of unsaturated acids are used as lubricating oil additives in the form of sulfurized esters (25, 26).

Esters of Higher Monohydric Alcohols

Esterification of higher alcohols from hexyl upward can be carried out conveniently, using stociometric quantities of alcohol and fatty acid under azeotrope conditions with benzene, toluene, or xylene as a solvent. Direct esterification of higher fatty alcohols is practical, using a stream of inert gas such as carbon dioxide, nitrogen, or even steam to sweep out the liberated water, or alternatively a partial vacuum may be used to remove water while retaining the acid and alcohol. Higher fatty alcohol esters of saturated acids are waxy solids.

Other Monohydric Esters

Vinyl esters are prepared in an unusual manner. Vinyl alcohol is unknown, but vinyl esters can be prepared by direct addition of acetylene to fatty acids at high temperatures, usually in the presence of a basic catalyst, such as zinc oxide (27, 28).

$$\mathrm{RCOOH} + \mathrm{HC{\equiv}CH} \xrightarrow{\qquad} \mathrm{RCOOH{=}CH_2}$$

An alternative process more suitable for laboratory preparation involves acidolysis of vinyl acetate with fatty acids in the presence of a mercury salt (29, 30, 31, 32).

Copolymerization of vinyl esters of saturated acids with vinyl acetate has been suggested for preparation of internally plasticized resins (33).

Teeter and Cowan prepared allyl, methallyl, and chloro-allyl esters by direct esterification and also by alcoholysis (34).

Tetrahydrofurfuryl and cyclohexyl esters have been prepared azeotropically, using benzene as a solvent (35). Tetrahydrofurfuryl oleate is marketed as a vinyl plasticizer.

Esters of Polyhydric Alcohols

Commercially the esters of polyhydric alcohols are far more important than the monohydric esters. In the case of monohydric alcohols it is possible to use a large excess of the esterifying alcohol, removing it at the conclusion of the reaction. With polyhydric alcohols this is impossible. With an excess of polyol the fatty acid residues are distributed randomly, leaving some free hydroxyl groups and giving a product containing all possible mono-, di-, tri-, etc., esters together with the fully esterified polyol. In order to carry esterification to completion it is necessary to use only the theoretical amount or a slight excess of the alcohol, using reaction conditions under which water is efficiently removed. Esterification by use of heat alone without special provisions for removal of water gives poor results both with respect to the rate and extent of esterification. Several methods are used for water removal:

1. *Azeotropic esterification.* The theoretical amounts of polyol and fatty acid are heated in the presence of refluxing xylene which carries away the water formed during the reaction. For laboratory preparations a simple trap such as the Dean-Stark or Bidwell-Sterling is used for collection of water. Measurement of the water distilled during reaction offers a convenient method for following the course of the reaction. The temperature of azeotropic esterification can be closely regulated by control of solvent quantity (36). Commercially azeotropic esterification is used, particularly for alkyd resin production. Phthalic anhydride sublimes readily at esterification temperature, and the azeotropic solvent (usually xylene) tends to dissolve and flush the sublimate back into the reaction kettle.

2. *Esterification using an inert gas sparge.* Rate and degree of esterification with polyols is improved by blowing an inert gas, such as carbon dioxide or nitrogen, through the reaction mixture (37, 38). Water is carried off by the gas stream, but losses of both polyol and fatty acid occur.

3. *Vacuum esterification.* Esterification under reduced pressure offers the most efficient and practical method for esterification with polyhydric alcohols (39, 40). A moderately rapid reaction is maintained at a lower temperature than for the other processes with good preservation of color. Glycerol, which is probably the most important polyol used for esterification, is moderately volatile at vacuum esterification temperatures. Partial condensers help minimize glycerol losses. A combination of vacuum esterification and sparging with CO_2 or even steam gives the most practical reaction from the standpoints of rate, completeness, and product color.

Catalysts can be used for speeding up esterification but usually to the detriment of color. Konen (41) in a study of the esterification of unsaturated acids with a series of polyols concluded that, in "quite an extensive study of catalysts, none was found that gave sufficiently good results to warrant use either commercially or in the laboratory. In all cases the use of a catalyst increased the initial esterification rate; but if a low final acid value (2-5) was desired, the time necessary to arrive at this acid value was the same with or without catalyst." There is an extremely voluminous literature on catalysis of the esterification reaction. Among catalysts which have been described are a variety of acidic materials, such as sulfuric acid, hydrochloric acid, phosphoric acid, sulfonic acids, Twitchell reagent, trifluoroacetic acid, boron trifluoride, alkyl acid phosphates, etc. Catalytic activity has been ascribed to practically all metals in the periodic table in the form of acetates, abietates, alkoxides, carbonates, chlorides, fluorides, hydroxides, oxides, naphthenates, and soaps of fatty acids. Metallic salts mentioned most commonly are lead, zinc, and calcium. Many of these esterification catalysts are also catalysts for alcoholysis, interesterification, and acidolysis reactions.

Good agitation during large scale esterification is of great importance. Paddle agitators are not normally satisfactory, and propeller or turbine types are needed to draw the heavy, fatty acid immiscible polyol from the bottom of the reaction vessel. This is particularly important in order to avoid charring with high melting polyols, such as pentaerythritol (42).

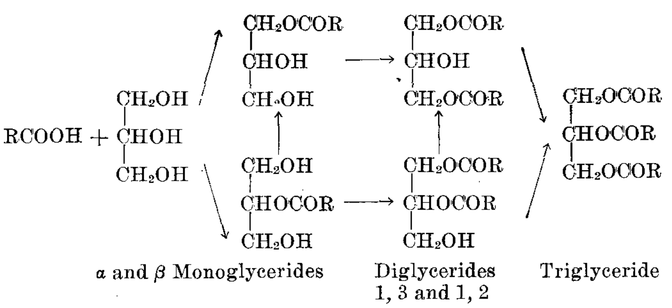
Esterification with Glycerol

Far more work has been devoted to the study of esterification of fatty acids with glycerol than with any other alcohol, either monohydric or polyhydric.

Lower molecular weight fatty esters are far less important than the higher fatty acid esters. Reaction of acetic anhydride with glycerol to form triacetin is used as a basis for the familiar "acetin" method for determination of this important polyol (43). Reaction of acetic anhydride with hydroxyl groups is used as an analytical determination for hydroxyl content (% hydroxyl, acetyl value, or preferably hydroxyl value) in oils and fats as well as in polyols (44).

Reaction of monoglycerides with acetic anhydride gives "aceto stearins," non-greasy, highly flexible fatty materials having promise as plasticizers, coatings for food products, and temperature-resistant spreads (45, 46, 47).

Esterification of glycerol is a stepwise process.



The primary initial product is the α monoglyceride although some β isomer also is formed but probably rearranges to the α-form. Similarly, the 1,3-diglyceride is the principal form on continued esterification leading finally to the completely esterified triglyceride.

The first comprehensive classical study of esterification of glycerol was carried out 100 years ago by Berthelot, who systematically prepared mono-, di-, and triglycerides from practically all fatty acids known at that time (48). Such esterification of fatty acids with glycerol is sometimes termed re-esterification since it gives the glycerides from which the acids and glycerol were originally derived.

Feuge, Kraemer, and Bailey studied the esterification of peanut oil acids with glycerol at 20 mm., using nitrogen sweeping and standardized agitation at various temperatures (49). The rate of esterification increases sharply with temperature (Figure 1). The reaction was found to be bimolecular but proceeded in two stages with heats of activation of 12,300 and 10,800 cal. per mole respectively.

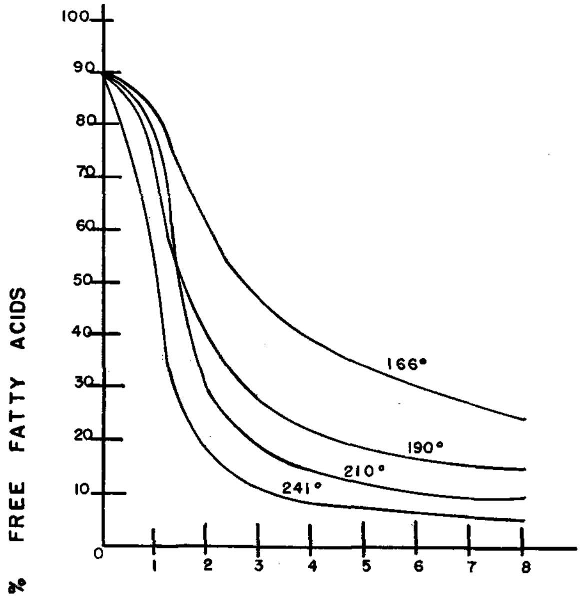


Fig. 1. Esterification of equivalent quantities of peanut oil acids and glycerol at various temperatures.

Experimental evidence indicates that the esterification of fatty acids gives a statistical or random distribution of fatty acids among the glyceride types. In the simplest sense, fats may be considered as composed of two acids, saturated and unsaturated. Figure 2 gives the composition of component triglycerides having s mole-fraction of saturated acids, S, and u mole-fraction of unsaturated acids, U.

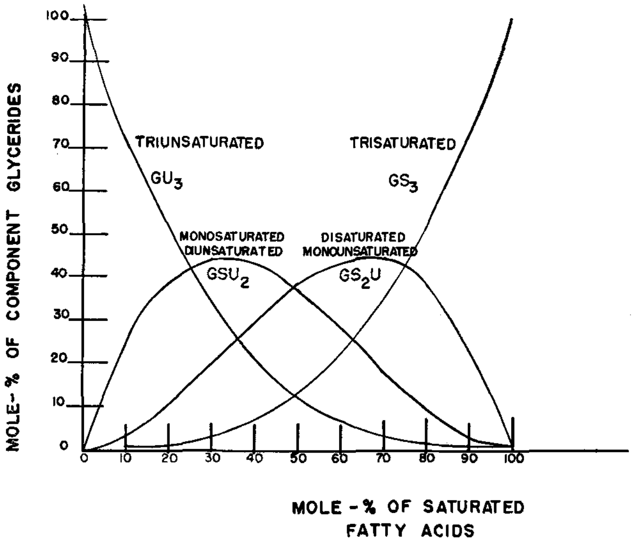


Fig. 2. Component glycerides at statistical distribution.

The composition of glyceride types is given by the following equations (49)[2]

Trisaturated, $GS_3 = s^3 \times 100$, mole-percentage.

Disaturated-monounsaturated, $GS_2U = 3s^2u \times 100$, mole-percentage.

Monosaturated-diunsaturated, $GSU_2 = 3su^2 \times 100$, mole-percentage.

Triunsaturated, $GU_3 = u^3 \times 100$, mole-percentage.

Bhattacharya and Hilditch esterified various combinations of saturated and unsaturated acids (50). The trisaturated glyceride content by permanganate oxidation fell very close to the trisaturated glyceride curve of Figure 2. Other studies involving interesterification of glycerides in homogeneous systems indicate that within experimental error the content of fully saturated glycerides corresponds to the amount calculated for random distribution (51, 52, 53).

Esterification of fatty acids with an excess of glycerol gives a mixture of mono-, di-, and triglycerides. The composition of the reaction mixture has been calculated on the basis of homogeneous reaction and

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[2] The above distribution is a special case of the generalized random distribution theory. With a mole-fraction of acid A, b mole-fraction of B, c mole-fraction of C, d mole-fraction of D, etc., glyceride types are as follows:

(All values as mole-percentage.)

Single component acid glycerides:

$GA_3 = a^3 \times 100$; $GB_3 = b^3 \times 100$, etc.

Two component acid glycerides:

$GA_2B = 3\,a^2b \times 100$; $GA_2C = 3\,a^2c \times 100$; $GAB_2 = 3\,ab^2 \times 100$, etc.

Three component acid glycerides:

$GABC = 6\,abc \times 100$; $GABD = 6\,abd \times 100$; $GBCD = 6\,bcd \times 100$, etc.

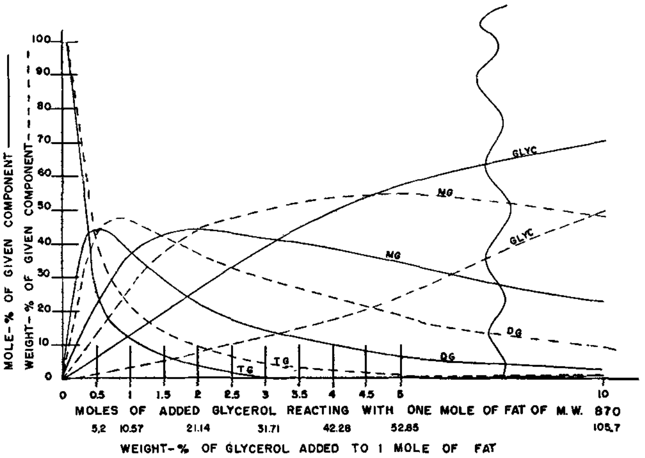


FIG. 3. Equilibrium between fats and glycerol assuming homogeneous reaction and statistical distribution.

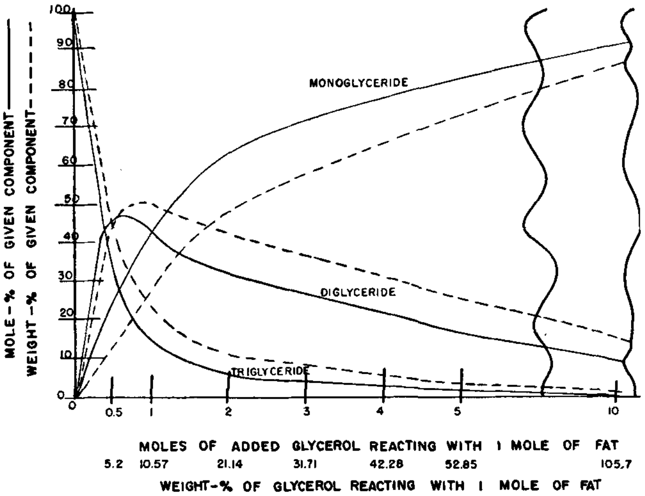


FIG. 4. Equilibrium between fats and glycerol after removal of excess glycerol.

(Assume homogeneous system and statistical distribution)

statistical distribution of fatty acids among available glycerol linkages (54). Figure 3 gives the statsitical composition on mole-% and weight-% bases for alcoholysis of a triglyceride of 870 M. W. (corresponding to soybean oil) by varying proportions of added glycerol. The figure also applies to esterification reactions, assuming complete esterification of a stoichiometric amount of glycerol followed by addition of excess glycerol over the range in Figure 3. Figure 4 gives the equilibrium composition of fatty components after glycerol removal. Normally the observed quantity of monoglyceride falls below the theoretical. For instance, Hilditch and Rigg (55) esterified fatty acid with excesses of glycerol up to 10 moles but obtained monoglyceride yields under 50% instead of the anticipated yield of approximately 85%.

The limiting factor determining the product composition is the comparative insolubility of glycerol in the reaction mixture. The reaction is homogeneous only over the lower ranges of glycerol addition. Feuge and Bailey determined experimentally the maximum quantity of glycerol which would react with and be soluble in hydrogenated cottonseed oil at various temperatures (54). Their results are given in Figure 5. The logarithm of the percentage of added glycerol is plotted against the temperature. Between the temperatures of 175°C. and 250°C. there is a linear relationship between the temperature and the logarithm of the maximum amount of glycerol in solution.

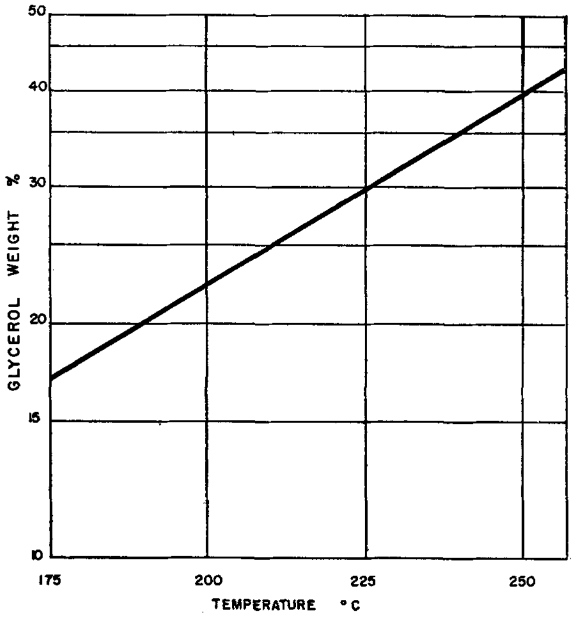


FIG. 5. Glycerol miscible and reactable with fat at various temperatures.

Referring back to Figure 4, at 175°C. the maximum content of glycerol which can be added while maintaining homogeneous reaction conditions is 17% corresponding to a maximum monoglyceride content of slightly over 40%. At 250°C. up to 40% of glycerol can be added to give a mixture at equilibrium containing 65% of monoglyceride. Practically, this temperature is too high, and intramolecular dehydration of glycerol or partial glycerol esters occurs to give polyglycerol and its esters (54, 56). Limiting temperatures of 200°C. to 225°C. are normally used, giving approximately 50% monoglyceride content as a maximum for technical monoglyceride either by direct esterification or by alcoholysis.

The data of Feuge and Bailey indicated that very close approach to the statistical distribution was obtained when lower levels of glycerol were used. Esterification of fatty acids by excesses of other polyols also has been demonstrated to give an approach to statistical distribution (57).

Addition of a mutual solvent permits higher monoglyceride content by maintaining homogeneous reaction conditions at high glycerol levels. Hilditch and Rigg (55) used phenol as a mutual solvent for esterification, and Eckey and Richardson used dioxane as a mutual solvent for glycerolysis (58). Mattil and Sims used pyridine as a solvent (59). In the reaction of fat with 50% by weight of glycerol in 4 parts of pyridine, using sodium methoxide as a catalyst at steam bath temperature, maximum conversions of monoglyceride of approximately 65% were observed. A 1:1 ratio of fats to glycerol gave a monoglyceride yield of 78%. These yields are close to the amounts predicted for statistical distribution in Figure 4.

Non-Glycerol Polyhydric Alcohol Esters

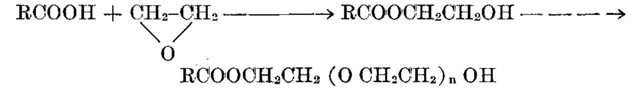
Non-glycerol esters are of very real importance, particularly for protective coatings. Goldsmith published a comprehensive literature review covering preparation, physical and chemical properties, and industrial applications of fatty esters of polyhydric alcohols (60).

Glycol esters are prepared by direct esterification as for glycerol esters with care to avoid loss of the more volatile glycol. Ethylene glycol, propylene glycol, and butylene glycol with other higher polyols are sometimes used as viscosity modifiers for alkyd resins. Propylene glycol maleates and phthalates have received recent attention as components of polyester resins for laminating and flexible foams.

Polyethylene glycols of general formula,

$$HOCH_2CH_2(O\ CH_2CH_2)_nOH,$$

where n has a value from 1 to approximately 15 are esterified to give surface-active monoesters and, using low molecular weight fatty acids, they give diesters which are vinyl plasticizers. Saturated esters marketed as polyoxyethylene stearate have been used as bread softeners, but their application for this purpose has been currently banned, pending accumulation of additional toxicity information. Although the monoesters may be prepared by direct esterification, a more elegant synthesis involves direct addition of ethylene oxide to the fatty acid in the presence of an alkaline catalyst (61).



$$RCOOH + \underset{O}{CH_2{-}CH_2} \longrightarrow RCOOCH_2CH_2OH \dashrightarrow RCOOCH_2CH_2\ (O\ CH_2CH_2)_n\ OH$$

A mixture of mono-, di-, tri-, tetra-, etc., ethylene glycol monoesters are formed, the mean chain length is determined by the molar ratio of fatty acid to ethylene oxide.

Higher polyol esters of unsaturated fatty acids are of particular importance in drying oil technology. The principal polyhydric alcohol is pentaerythritol, but a wide range of polyols has been considered.

When highly unsaturated fatty acids are esterified with polyhydric alcohols, especially alcohols having more than three reactive hydroxyl groups, the resultant ester will polymerize if temperatures are too high. The polymerization can lead to high viscosity or even gelation before an adequate reduction in acidity is attained. Konen, Clocker, and Cox (41) esterified linseed acids with a group of polyols and selected 232°C. (450°F.) as an optimum temperature. At higher temperatures the rate of polymerization increased quite sharply without appreciable increase in the rate of esterification. Figure 6 illustrates the esterification of linseed acids with several polyols, using vacuum-processing at 232°C. with a stoichiometric amount of polyol. The rate of esterification is a function of the type of hydroxyl groups. Pentaerythritol and dipentaerythritol having only primary hydroxyls esterify most rapidly. Glycerol having two primary and one secondary hydroxyl esterifies more slowly. Sorbitol has six hydroxyls, two primary and four secondary, but under esterification conditions internal dehydration occurs and from a practical standpoint only four hydroxyls are available, one primary and three secondary. In line with the hydroxyl type this polyol esterifies still more slowly. Specific papers cover esterification of pentaerythritol (42), dipentaerythritol (62), and sorbitol (63). Both sorbitol monoesters and sorbitol monoesters reacted further with ethylene oxide are marketed as nonionic surface-active agents.

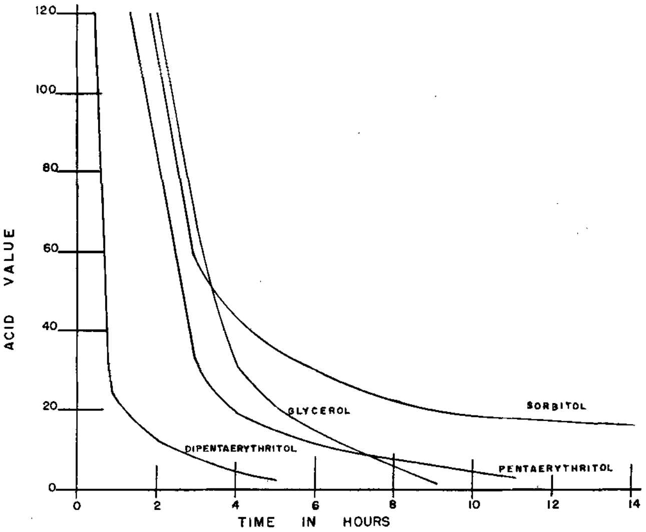


FIG. 6. Esterification of linseed fatty acids with stoichiometric quantities of glycerol, pentaerythritol and dipentaerythritol at 232°C. and with sorbitol doing a 4:1 molar ratio of fatty acid to polyol.

The esterification of erythritol (41, 42, 64), trimethylol propane (42), and inositol (64, 65) have been considered in papers dealing primarily with other polyols. Tetramethylol cyclohexanol (TMC), a pentahydroxy alcohol derived from reaction of formaldehyde with cyclohexanone, shows an initial rate of esterification similar to glycerol during the stage of primary hydroxyl reaction. During later stages of reaction the secondary hydroxyl of glycerol esterifies more rapidly than the hindered secondary hydroxyl of TMC (66).

Xylitol (67, 68), alpha methyl D-glucoside (65), and the hexitols, inositol (69), pinitol, and quebrachitol (64), have all been esterified with drying oil acids. The latter paper (64) compares esterification of a number of polyols, using xylene as an azeotrope.

Sugar esters cannot be prepared by direct esterification because of caramelization of sugar at normal esterification temperatures. Fatty acid chlorides in tertiary amines have been used for preparation of such esters (70).

Polyvinyl alcohol esters cannot be prepared directly because of the insolubility of the polyol in fatty acids. Rheineck used phenol as a mutual solvent for esterification (71). Polyvinyl esters have also been prepared by interesterification of methyl esters and vinyl acetate (72).

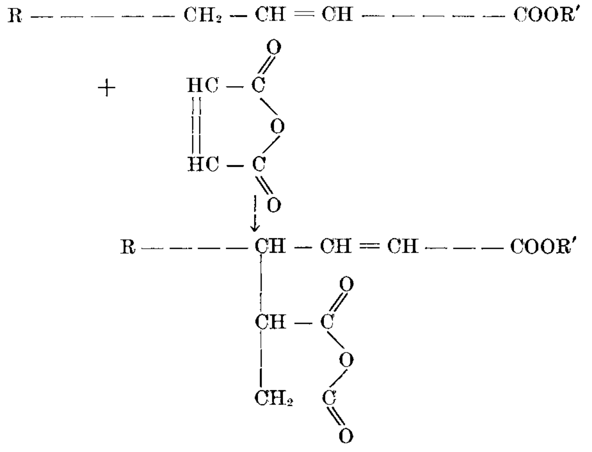
Phosphite esters have been described as catalysts for esterification of phenolic resins with fatty acids (73). Similar catalysts have been claimed as color-stabilizers in esterification of dibasic acids (74). Kinetics of esterification of poly-alcoholic resins with fatty acids have been reviewed by Rubin (75).

Esterification of tall oil presents a difficult problem because of the drastic conditions required to accomplish reaction of the rosin acids. Dunlap investigated the selective esterification of tall oil, using glycerol and pentaerythritol (76). Both fatty acid acidity and rosin acid acidity were determined during the esterification at various temperatures of a tall oil having approximately half of its acidity as fatty acids and half as rosin acids. Results are shown in Figure 7.

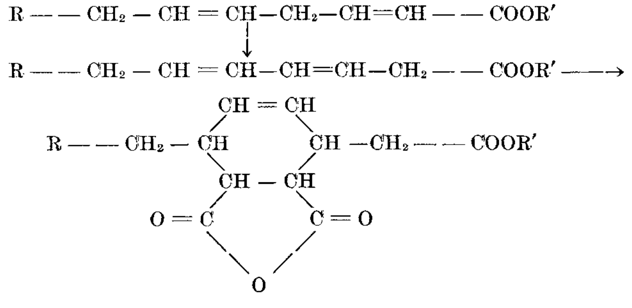
At 180°C. virtually all reduction in acidity is accounted for by esterification of fatty acids, and reaction of rosin acids is negligible. At 220°C. esterification of fatty acids occurs primarily, with limited esterification of rosin acids. At 250°C. and 275°C. there is relatively little change in the rate of fatty acid esterification, but appreciable reaction of rosin acids takes place. In order to prepare tall oil esters of low acidity (5-10 A.V.) it is necessary to operate at high temperatures (240°-260°C.) during the latter part of the esterification, using an appreciable excess (10-20%) of polyol to counteract the effect of polyol decomposition and intermolecular dehydration (77, 78).

Tall oil esters are used in protective coatings and particularly in foundry core binders in conjunction with petroleum resins. Esterification of rosin acids under similar esterification conditions with glycerol gives ester gum and with pentaerythritol gives PE ester gum. Modification may also be carried out, using maleic anhydride as an acid to give a series of varnish and lacquer resins.

Esterification of combinations of fatty acids and phthalic anhydride with polyols gives the familiar and very important oil-modified alkyd resins. Closely related is the production of maleic modified oil (79). Maleic anhydride adds to unsaturated fatty acids or esters probably to form alkenyl succinic anhydrides (80, 81).



Simultaneously under conditions of addition at 200-240°C., there may be some conjugation of fatty acid unsaturation followed by Diels-Alder type addition to the conjugated structure.



Esterification of the maleic adducts of glycerides with polyols is carried out, using vacuum processing or by azeotropic esterification. Because of the tremendously increased functionality of the maleinized oils, caution must be exercised during esterification to avoid excessive viscosity increase before the acidity is reduced to a desirably low level.

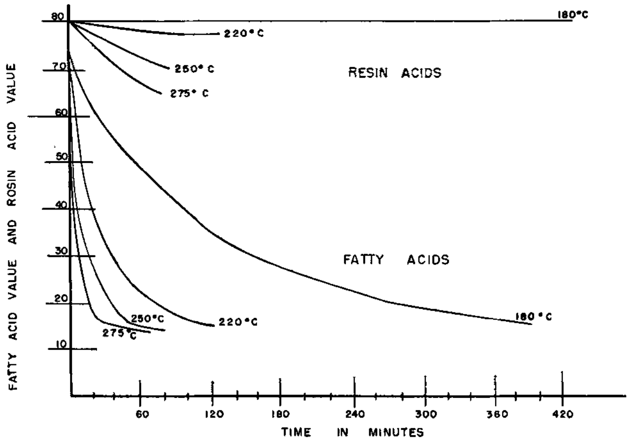


FIG. 7. Esterification of fatty acids and rosin acids at various temperatures, using 10% excess of pentaerythritol.

An alternative method for preparation of maleic modified oils involves alcoholysis of the oil with a polyol (usually glycerol or pentaerythritol), followed by esterification with maleic anhydride (82).

Alcoholysis

Alcoholysis is the most common of the exchange reactions and was applied as early as 1846 when Rochleder described the preparation of glycerol by ethanolysis of castor oil (83). Alcoholysis is catalyzed by a variety of materials of which the alkali metal alkoxides are most effective. Technically, the alcoholysis of fats with polyol, such as glycerol and pentaerythritol, is a common procedure in the manufacture of oil modified alkyd resins. Catalysts effective in promoting alcoholysis are also effective in interesterification reactions.

Alcoholysis by Monohydric Alcohols

The mechanism of alcoholysis of glycerides by monohydric alcohols was investigated by many early workers, who demonstrated that the reaction is catalyzed by both acids and bases (84, 85, 86). The reaction is very rapid in homogeneous systems in the presence of alkaline catalysts. Reid concluded that alcoholysis using sodium alkoxides took place approximately 4,000 times as fast as alcoholysis using an equivalent amount of HCl (87). During the course of the saponification-value determination, using alcoholic alkali, alcoholysis proceeds far more rapidly than saponification with the result that the alkali reacts primarily with ethyl esters rather than triglycerides (88). Anderson and Pierce concluded that alcoholysis is about 1,500 times as fast as saponification (89). As an indication of the speed of the alcoholysis reaction Feuge and Gros in an investigation of the ethanolysis of peanut oil reported that turbidity, because of glycerol separation, occurred within 1.5 min. after addition to the oil of alcoholic alkali containing 2 equivalents of ethyl alcohol and 0.2% of NaOH based upon the oil (90). An optimum temperature of 50°C. was observed, and reaction proceeded rapidly at lower temperatures.

In the methanolysis of oils at moderately low temperatures smaller proportions of methyl alcohol give higher conversions to methyl ester because of the favorable effect of glycerol precipitation, which would remain in solution using higher proportions of methyl alcohol (91).

Wright studied alcoholysis of methyl ester by higher alcohols, such as furfuryl, tetrahydrofurfuryl, benzyl and methyl cellosolve, removing the liberated methyl alcohol by distillation (4). Using lead soaps as catalysts, relatively high temperatures of 200°C. were required in alcoholysis of glycerides, which proceeds readily even at room temperature with alkali metal hydroxides.

The alcoholysis procedure is normally much simpler than esterification for preparation of lower alkyl esters. In some cases it permits ester formation which could not be accomplished by direct esterification. For instance, furfuryl alcohol cannot be esterified directly in the presence of acid catalysts because under these conditions rapid polymerization of the alcohol takes place. Alcoholysis of oils with furfuryl alcohol proceeded readily, using 0.5% of sodium metal as a catalyst (92).

Methanolysis of triglycerides, using an anion exchange resin, has been suggested (93), and cation exchange resins have also been checked but found to be relatively ineffective (94).

The alcoholysis of fats and oils with low molecular weight alcohols, followed by distillation of the ester fraction, has been suggested for concentration or purification of vitamins and sterols (95). Alkyl esters have been suggested as intermediates in soap making (96). The alcoholysis procedure permits relatively simple recovery of glycerol in higher concentrations than are obtained in regular aqueous saponification.

Alcoholysis by Polyhydric Alcohols

Alcoholysis of fats and oils with polyhydric alcohols is far more important technically than reaction with monohydric alcohols. Acidic materials are quite ineffective as catalysts, and reaction in the absence of catalyst is inappreciable at practical operating temperatures. For instance, alcoholysis of soybean oil with pentaerythritol in the absence of catalyst required a temperature of 280°C. (42). Alkali metal hydroxides, carbonates, and alkoxides are very effective as catalysts, and the oxides and oil-soluble soaps of calcium, barium, lead, lithium, zinc, cadmium, and strontium are somewhat less effective but may present some advantages in color of products. Because of the relative insolubility of higher polyol in fats it is necessary to operate at relatively high temperatures of 200-230°C. in order to maintain homogeneous reaction conditions.

Alcoholysis with glycerine is an important industrial reaction for preparation of a variety of partial esters. Sodium hydroxide has been a favored catalyst for alcoholysis to give edible products (97, 98) whereas calcium oxide and litharge, which give calcium and lead soaps, are favored for alcoholysis during manufacture of alkyd resins and modified drying oils. As alcoholysis proceeds to give a mixture of glycerol and mono-, di-, and triglycerides, the product becomes progressively more soluble in polar solvents. Solubility in 4 to 5 volumes of methyl or ethyl alcohol is frequently used as a criterion for completeness of alcoholysis.

Feuge and Bailey demonstrated that the glycerolysis of triglycerides in the presence of sodium hydroxide as a catalyst gave essentially statistical distribution of mono-, di-, and triglyceride (54). Figure 3 illustrates such composition. As was pointed out in the discussion of esterification of fatty acids by glycerol, the limiting factor in determining the composition of the reaction mixture is the solubility of glycerol at reaction temperature. Dioxane and tertiary amines have been used as a mutual solvent to permit higher monoglyceride yields (58, 59).

If the homogeneous alcoholysis mixture containing alkaline catalyst is cooled slowly, glycerol separates, upsetting the equilibrium composition. Re-equilibration occurs to give a new distribution of partial esters corresponding to the amount of glycerol remaining in the solution phase. During gradual cooling in the presence of catalyst the quantity of monoglyceride can be seriously reduced. It was pointed out that addition of strong phosphoric acid at the optimum alcoholysis temperature destroys the alkaline catalyst and permits maintenance of maximum monoglyceride content during cooling (99, 59).

At high temperatures monoglycerides decompose to give glycerol, and under vacuum steam-distillation conditions glycerol can be removed nearly completely, leaving a still residue of triglyceride. The decomposition is accelerated by traces of alkaline catalysts and to a lesser extent by acids. Arrowsmith and Ross report that, if an alcoholysis mixture is carefully adjusted to a pH of 6-7, the monoglycerides in a technical monoglyceride (approximately 50% monoglyceride content) can be distilled under vacuum (100, 101). Distillation using normal high vacuum technique has been extended commercially to molecular distillation (102). Starting with a technical product containing 40-50% of monoglyceride, distillates of 90-97% monoglyceride content can be obtained at sufficiently low temperatures and in a sufficiently rapid time to limit decomposition. By use of three stages of centrifugal short-path distillation Kuhrt reports that almost instantaneous removal of monoglyceride is observed with limited decomposition (103). The time factor is important since it was indicated that at 100°C. a 10% loss in monoglyceride content required a heating period of more than 8 hours whereas at 230°C. 10% reversion will occur in as little as 5 min.

Alcoholysis of glycerides by other polyols utilizes essentially the same procedures developed for glycerol. Burrell (42) studied the pentaerythritolysis of linseed and soybean oils. A variety of metal salts as naphthenates, stearates, or abietates were examined as catalysts at a 1% level in the alcoholysis of soybean oil with 24% of pentaerythritol at 230°C.

The solution of pentaerythritol in the reaction mixture was taken as an end-point to indicate alcoholysis and was found to correspond closely to the familiar alcohol solubility test. Calcium naphthenate was particularly effective, giving clarity in 5 min. with better color than could be obtained using lead naphthenate or litharge. Burrell then compared the reactivity of various polyols in the alcoholysis of soybean oil at 230°C., using 1% of calcium naphthenate.

The speed of alcoholysis appears to be partially a function of type of hydroxyls; the primary reacts more rapidly than the secondary. The rate is also undoubtedly a function of polyol solubility in oil.

Polyol used	Alcoholysis time in min.
Trimethylol propane	0.5
Ethylene glycol	1.0
Tetraethylene glycol	2.0
Pentaerythritol	5.0
Glycerol	6.0
Mannitol	Not in 4 hours
Polyvinyl alcohol	Not in 4 hours
Sucrose	Not in 4 hours

Partial replacement of glycerol by a higher polyol can be obtained under conditions of vacuum-distillation. Wright obtained partial replacement of glycerol by pentaerythritol, by heating under vacuum at 200-250°C. in the presence of a lead salt catalyst (4). Preparation of pentaerythritol esters (4, 104) and glycerol esters (68) from methyl esters by alcoholysis has also been described.

Acidolysis

Acidolysis, the replacement of an acyl group of an ester by the acyl group in an acid, is less important than the other ester exchange reactions. Early literature reported that lower molecular weight acids tend to replace higher acids, but later investigation indicated that there is little tendency for one acid to be more active than another in acidolysis. The equilibrium constant is 1.0 even with acids as widely separated as acetic and stearic (106). Reaction of acetic acid with coconut oil, using sulfuric acid as a catalyst, gives mixed aceto glycerides which are reported to be nitrocellulose plasticizers (107). Introduction of butyric acid into tallow by acidolysis followed by re-esterification of glycerol, has been suggested for preparation of butter-like fats (108).

Triglyceride compositions can be modified by acidolysis reactions by heat alone or in the presence of zinc oxide, using vacuum distillation to remove lower molecular weight acids (109). When a mixture of palm acids and palm oil are heated under vacuum distillation conditions, acidolysis occurs and the lower-molecular-weight palmitic acid is removed by distillation from the 18 carbon acids. A similar reaction is suggested for upgrading of fish oil and soybean oil for coating purposes. Analogously, vacuum-distillation of a mixture of oils and dimer acids from heat polymerization results in replacement of monomeric acids and improvement of quality for coating application (129).

Kaempfe reports improved heat polymerized fish oil by blowing with steam at temperatures above 260°C. (110). Hydrolysis, followed by acidolysis, apparently occurs. Fish oils contain about 25% of saturated acids, chiefly palmitic, together with C_{18-24}, and even higher-molecular-weight unsaturated acids. Preferential removal of palmitic acid improves the bodied oil for coating use.

Acidolysis occurs during varnish cooking in which glycerides are heated at temperatures of 260-315°C. with acidic resins (111, 112, 113, 114). Retardation of gelation of tung oil by rosin is ascribed to the acidolysis reaction in which resin acids enter the glyceride structure.

Monomeric vinyl esters have been prepared from fatty acids and vinyl acetate using mercury salts as catalyst (29, 30, 31, 32).

Interesterification

Friedel and Crafts first recognized the interesterification reaction in 1865 (115). Historically, this first described interesterification was a thermal non-catalytic interchange between ethyl benzoate and amyl acetate. Interesterification involving glycerides was not recognized until the 1920's when Van Loon (116) and Normann (117) independently demonstrated that the reaction could be effected by merely heating oils and fats at high temperatures or more readily at lower temperatures in the presence of catalysts.

The distribution of fatty acids in naturally occurring glycerides is selective rather than random. The quantities of trisaturated glycerides present in seed fats, especially, falls considerably short of the statistically expected quantity. Referring to Figure 2, cottonseed oil containing approximately 25% of saturated acids should have 1.6% of trisaturated glycerides according to statistical distribution, but it contains at most a few tenths of 1% of the fully saturated glycerides. Cocoa butter containing 60% of saturated acids should have 22% of trisaturated glycerides but contains only a few per cent. In classical research studies Hilditch investigated the relative distribution of saturated and unsaturated acids in a large variety of natural fats and oils and proposed his "Rule of Even Distribution" to explain the observed glyceride distribution (118). More recently, Kartha proposed the "Rule of Glyceride Type Distribution," which, based upon relatively simple analytical data, permits calculation of glyceride composition based on statistical formulas (119). Interesterification of natural triglycerides at temperatures above the fat melting point shifts the distribution of component glycerides from the observed selective orientation to a statistical or random arrangement (51, 120).

A variety of metallic salts, oxides, and hydroxides have been described as interesterification catalysts. These are relatively ineffective, requiring rather high temperatures with consequent thermal breakdown. The reaction between ethyl benzoate and benzyl acetate of Friedel and Krafts proceeded slowly at 200-250°C. and required a temperature of 300°C. to give an appreciable rate of interchange (115). Normann found that at least 24 hours at 250°C. were required to give relatively complete interchange equilibrium of a mixture of 10 parts of tristearin and 90 parts of soybean oil (117). Even at 270°C. Van Loon found that more than 8 hours were required to reduce the melting point of a mixture of beef stearine and soybean oil to its final melting point (121). Hilditch heated synthetic beta oleodistearine at 300°C. for 10 hours to give an equilibrium mixture of tristearin, distearoolein, monostearodiolein, and triolein (122). Earlier catalysts, such as tin and stannous hydroxide, permit reduction in temperature and time but are far less effective than alkali metal derivatives. Norris and Mattil (52) reacted mixtures of synthetic triolein and tristearin in the presence of stannous hydroxide, first introduced by Van Loon (116, 121), for 1 to 3 hours at 225°C. to obtain a mixture containing trisaturated glycerides corresponding to statistical distribution within experimental error of their crystallization analysis procedure.

The most effective catalysts for interesterification are alkali metal derivatives of extremely weak acids (51, 123). Included in this category are alkali metal alkoxides, alkyls, and aryls. Alkali metals themselves (as powder dispersion in solvents) (123) and alkali metal hydrides (124) are also highly effective, probably reacting with free hydroxyl groups in fats to form complex alkoxides. With such catalysts random distribution is obtained in a matter of minutes at low temperatures of 50-60°C. Appreciable catalytic activity is even observed at sub-zero temperatures.

The reactants in esterification, alcoholysis, and acidolysis reactions are all catalysts for interesterification although they are relatively inefficient and function only at relatively high temperatures. A small amount of water (125) hydrolyzes triglycerides to give fatty acid and diglyceride. If re-esterification occurs, involving a different fatty acid from the one originally split off, a new ester is formed together with water, which can go through the hydrolysis-esterification cycle. Volatility of water under atmospheric pressure limits the potential of this reaction, but in an autoclave at high temperature it represents an effective method for interesterification. The alcohol split off (a diglyceride in the case of fat hydrolysis) may react with a triglyceride by way of the alcoholysis reaction to form a different triglyceride and a new diglyceride. Use of monoglycerides for catalysis of interesterification, particularly in the presence of alkaline catalysts, has been described by several investigators (126, 127, 128). Similarly, the acid may displace a different fatty acid from a triglyceride to form a new glyceride molecule, liberating a different fatty acid to continue the interchange reaction.

Such interesterification through the acidolysis reaction is of particular importance during heat bodying of oils. Fatty acids are liberated partially through hydrolysis and partially through cracking and thermal breakdown. Simultaneously the polyethenoid acids undergo polymerization chiefly to give dimers although higher polymers are also formed. Interchange of acyl groups between glycerides and liberated acids produces new esters and new acids until ultimately a random or statistical distribution of saturated acids, unpolymerized unsaturated acids, and polymerized acids is obtained on glyceride molecules (126, 129, 130, 131).

Directed Interesterification

In the absence of a directing influence, interesterification can give only a statistical glyceride distribution. This reaction is commercially important in the case of lard. Lard has a narrow plastic range, that is, there is a relatively short temperature range in which lard has good working properties as a shortening. Above this range the consistency is too soft and below, lard is too firm. Lard creams poorly and gives poor cake volume (132). Interesterification of lard widens the plastic range, increases creaming and cake volume and improves appearance (133, 134, 135). The rearrangement of lard coupled with application of butylated hydroxyanisole as an antioxidant makes lard more competitive with hydrogenated vegetable shortenings.

Several methods have been described for obtaining non-statistical orientation. The "Directed Rearrangement" process of Eckey (51, 123), in which interesterification takes place with simultaneous crystallization, represents a particularly valuable extension of the interesterification reaction. If a liquid reaction mixture of a glyceride and an alkaline catalyst (sodium alkoxide, sodium metal, sodium hydride, etc.) is gradually cooled, the least soluble component, trisaturated glyceride, crystallizes from the reaction mass. This removal of an insoluble component upsets the equilibrium, and more trisaturated glyceride is formed in an attempt to reproduce statistical distribution in the homogeneous liquid phase. Precipitation continues as determined by the solubility of the fully saturated glycerides at the final reaction temperature. For oils such as cottonseed and menhaden, containing approximately 25% of saturated acids, as much as 18 to 24% of the total acids of the oil can be separated as trisaturated glycerides in an interesterification period of approximately one week at gradually lowered temperatures down to 10°C. If such an interesterified product is warmed in the presence of the catalyst to a temperature above the melting point, the mixture reverts to statistical distribution. In order to retain the directed distribution with high content of fully saturated glycerides, the catalyst is destroyed at low temperature by addition of acids or water. Subsequent washing, crystallization (with or without solvent), and filtration separates the interesterified oil into a solid fraction, having a high saturated acid content and low iodine value, and a liquid fraction, having a lower saturated acid content and a higher iodine value.

Application of this directed interesterification with subsequent separation of solid glycerides has potential value for upgrading of drying oils. Soybean oil, for instance, contains about 14-16% of saturated acids, which are held almost without exception on glycerides containing two unsaturated acids (136). On a mole % basis about 45-50% of soybean oil consists of these monosaturated-diunsaturated glycerides, which during drying can form only linear polymers if it is assumed that each unsaturated acid has a functionality of only one. By removal of all of the saturated acids the iodine value of soybean oil would be raised from an average value of approximately 135 up to approximately 160. In practice the maximum iodine value practically attainable is about 148 to 154. This requires appreciable removal of saturated acids and results in an oil of improved drying potential.

In another modification of the same principle of interesterification with precipitation of glyceride, alkaline catalyst is added to chilled oils containing a solid crystalline grain (137, 138). In the case of most oils the crystals present in the chilled product contain a preponderance of disaturated-monounsaturated glycerides, and these act as crystal nuclei or seed influencing subsequent interesterification to give continuing separation of the disaturated-monounsaturated glycerides. With long storage there is gradual re-solution of the disaturated glycerides and precipitation of the less soluble trisaturated glycerides. The method has potential value in the edible oil field for production of margarine oils and puff pastes, but there is only limited potentiality in the drying oil field since the conversion of saturated acids to insoluble glyceride forms does not proceed to a sufficient extent to remove a large proportion of the saturated acids.

A closely allied reaction involves alcoholysis under conditions similar to those used in the directed interesterification. If glycerol is added to an oil which is undergoing interesterification, the process becomes a mixed one of alcoholysis and interesterification since the same catalysts are active for both reactions (139, 140, 141). This ester-alcohol exchange produces an equilibrium mixture containing glycerol, monoglyceride, diglyceride, and triglyceride. At lower levels of glycerol up to 5% selective crystallization of diglyceride takes place, and at higher glycerol levels of 10% quite pure monoglyceride precipitates. At an intermediate level both partial esters separate. This selective precipitation of partial glycerol esters is more nearly complete than the triglyceride precipitation and permits removal of virtually all saturated acids from the rearranging fat.

Directed interesterification reactions can also be effected by removal of a volatile component. Trieleostearin cannot be prepared by direct esterification of the acid with glycerol since polymerization occurs simultaneously with esterification. The glycerol ester can be prepared by interesterification of methyl eleostearate and triacetin in the presence of sodium methoxide under vacuum (41). As methyl acetate is formed by the interchange, it is removed, ultimately giving relatively pure trieleostearin. In an analogous way Eckey prepares fatty polyvinyl esters by interesterification between polyvinyl acetate and methyl esters of fatty acids (72).

A somewhat related displacement is obtained when methyl esters of higher molecular weight acids are heated with glycerides of lower average molecular weight in the presence of an interesterification catalyst (142, 143). Lower molecular weight methyl esters are removed by vacuum-distillation, leaving a glyceride of changed composition.

Interesting possibilities exist for interesterification involving combinations of fats or combinations of fats with simple esters. Tung oil is subject to crazing and wrinkling during film drying unless it has been heat treated partially to isomerize and polymerize the eleostearic acid. This drying defect is probably caused by trieleostearin, which would statistically be present to an extent of not less than 60%. Simple blends of tung oil and soybean oil which might be used in house paints also showed this deficiency in the dried films. By interesterification to give a redistribution of tung acids and soybean acids, "gas-proofing" can be attained at low temperatures. A simple blend, for instance, of 1 part of tung oil and 2 parts of soybean oil, would contain approximately 20% of trieleostearin. An interesterified mixture of the same composition would contain only 2.3% of trieleostearin, an amount insufficient to affect film characteristics. Such interesterified tung-soybean combinations were marketed for house paint use when both tung and soybean oils were lower in cost than linseed oil. Calcium soaps have been preferred catalysts for such reactions, and Reutenauer suggested interesterification of linseed oil with rape and safflower oils as a means of extending linseed oil supply during periods of shortage or high cost (144).

Fats can be interesterified with simple esters such as acetates, butyrates, etc., to give mixed glycerides. There is both industrial and edible significance for such modifications. Interesterification between fat triglycerides and triacetin may be used for preparation of acetoglycerides (46, 47). Use of a large excess of triacetin (0.5 parts per part of fat) gives primarily diaceto glycerides, waxy, translucent fats having promise as plasticizers, high temperature spreads, and edible protective coatings for foods.

Although interesterification was recognized long ago, it has only been in recent years that intensive study has been given to the reaction as a means of modification of fats and oils. Very real potential exists for more widespread industrial application of this method.

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Nitrogen-Containing Derivatives of the Fatty Acids

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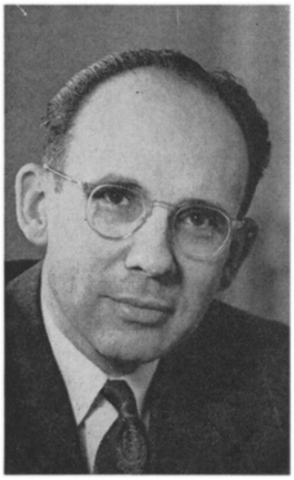

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THE chemical literature describes the application of almost all reactions of organic acids to the higher fatty acids. Among these reactions are many by means of which the nitrogen atom is introduced into the molecule. Although the present discussion will emphasize those processes which are applied commercially, many other typical reactions will be mentioned.

Within the past two decades an important industry has developed based upon derivatives of the higher fatty acids which contain nitrogen. To a very large extent the usefulness of these products results from the properties imparted by the nitrogen atom, in combination with the hydrocarbon chain. Generally these useful properties can be described in terms of the surface activity of the molecule. Frequent references to this property will be made throughout the following discussion.

Usually nitrogen is introduced into the fatty-acid molecule through the reaction of the carboxyl group with ammonia or amines. By this means are obtained amides and nitriles and, from these, amines and quaternary ammonium salts. Modifications and derivatives of these major classes make up the greater proportion of the material to be presented here. Methods of preparation and chemical reactions of various derivatives will be discussed. Properties and uses will be mentioned briefly.

Throughout the following discussion chemical reactions will be presented in general terms. The symbol R will be used to designate either saturated or unsaturated normal aliphatic chains.

Amides

Simple amides are produced through the reaction of a molecule of fatty acid and a molecule of ammonia with the elimination of one molecule of water (1):

$$RCOOH + NH_3 \longrightarrow RCONH_2 + H_2O$$

This process is employed for the commercial preparation of the higher aliphatic compounds. The fatty acids are heated in a closed vessel to a temperature of about 200° and are then subjected to a stream of ammonia gas under slight pressure; continuous venting removes excess ammonia and water as it is formed. The resulting product consists of approxi-