Esterification of Unsaturated Fatty Acids[1]

J. C. KONEN, E. T. CLOCKER and R. P. COX
Archer-Daniels-Midland Company
Minneapolis, Minn.

THE two most commonly used textbook definitions of an ester are: 1. An ester is an alkyl salt. 2. An ester is the product formed by the reaction of an alcohol with an acid. Both of these definitions leave much to be desired. No. 1 would not include esters of cyclic alcohols. No. 2 is not valid since esters may be formed by several methods other than the reaction of an alcohol with an acid.

It would seem more suitable, therefore, to define an ester as a material which, on hydrolysis, yields an alcohol and an acid. There are four generally used direct methods and two indirect methods of forming esters:

1. The reaction of an alcohol and an acid with the elimination of water.
2. The reaction of an acid anhydride and alcohol.
3. The reaction of an acid chloride with an alcohol with elimination of HCl.
4. The reaction of an alkyl halide with a salt of an organic acid with elimination of a salt.
5. The indirect methods are alcoholysis and ester interchange.

Alcoholysis is often incorrectly termed ester interchange and consists of the replacement of one alcohol by another. An example would be the reaction of methyl alcohol with a glycerol ester to form a methyl ester. Glycerol is eliminated and easily separated. This reaction was covered by Wright and his coworkers in a recent publication (7).

True ester interchange is similar to the double decomposition reaction of inorganic chemistry. An example of commercial usage would be the interchange which takes place when ester gum (glycerol abietate) is properly heated with linseed oil in the cooking of varnish.

To digress a moment, we would like to cite the use of this method for the preparation of pure eleaostearic esters (5). This acid is so reactive that it is impossible to esterify it by common methods without gelation before the reaction is completed. However, by the ester interchange method, it was possible to obtain a limpid oil that contained no free fatty acids.

The reaction was carried out as follows: .05% of dry sodium methylate was dissolved in 1 mol of anhydrous neutral glycerol acetate. This was then mixed with 3 mols of neutral methyl eleaostearate. Methyl acetate was distilled off under vacuum in a closed system at 60°-100° C. The resulting glycerol tri-eleaostearate was washed with ethyl alcohol to remove the small amount of soap present. Pure glycerol tri-eleaostearate resulted.

Of the methods of ester formation outlined above we will confine our discussion to the first type mentioned—direct reaction of fatty acids with an alcohol. The mere mixture of an alcohol with a long chain fatty acid will give no reaction, but if a strong acid is added as a catalyst, the reaction proceeds readily.

Water is formed, and soon a state of equilibrium is reached. This is governed by the rate of hydrolysis of the ester in the presence of water. In order to cause the reaction to go to completion, water must be removed. In the case of a water soluble alcohol this may be done by addition of a solvent and azeotropic distillation. If a water insoluble alcohol is used, the water may be distilled off azeotropically if a large excess of alcohol is used. In general, the best way of forming esters of monohydric alcohols is by alcoholysis using metallic sodium or NaOH or KOH as the catalyst (2, 4).

In the case of monohydric esters it is possible to use an excess of alcohol, but with polyhydric alcohols this is impossible. If an excess were used, the fatty acid molecules would distribute themselves evenly and free hydroxyls would be left, some mono- and some polyesters being formed. To carry the esterification to completion then the theoretical, or only a slight excess, amount of alcohol must be used and the water of reaction removed efficiently.

This may be done in several ways: If color is not of prime importance, esterification can be carried out by combining the theoretical quantity of fatty acids and polyhydric alcohol in the presence of a catalyst and esterifying in the presence of refluxing xylene which will carry off the water formed during reaction. The use of a water absorbing material, such as anhydrous copper sulfate, will remove the water formed during the reaction and promote ester formation. Attempting to esterify fatty acids and polyhydric alcohols using heat alone gives very poor results, both as to extent of ester formation, rate of reaction and loss of ingredients.

BOTH the rate and degree of esterification of fatty acids with polyhydric alcohols can be improved by blowing an inert gas, such as carbon dioxide or nitrogen, through the reaction mixture at some optimum temperature. Water is carried off by the stream of gas, but so are large quantities of fatty acids and polyhydric alcohols.

Esterification under reduced pressure is probably the most efficient method for preparing fatty acid esters of polyhydric alcohols, promoting a fairly rapid reaction at a lower temperature, and maintaining the best possible color. Glycerol, which is probably the most common alcohol used, distills quite readily under vacuum and if any water is present, it is removed with the alcohol. In order to prevent undue loss of glycerine an air-cooled column is introduced into the system, which condenses glycerol allowing the water to pass on through to the receiver. Under these conditions alcohol loss is held to a minimum, and the process can be economically used for the commercial production of synthetic esters. Combining vacuum esterification with esterification in the presence of an inert gas improves this process, the inert gas being a source of agitation as well as a medium for the more rapid removal of water.

When unsaturated fatty acids are esterified with polyhydric alcohols, especially those having more than three hydroxyls, the resulting ester will polymerize rapidly if the reaction temperature is too high. Such

---

[1] Presented before the American Chemists' Society Meeting, Chicago, Illinois, 1944.

polymerization may result in gelation before a sufficiently low acid value is reached. In order to determine the optimum temperature of esterification a number of runs were made at various temperatures. It was determined that at 450° F., the rate of esterification in relation to rate of viscosity increase was optimum. Above 450° F. the bodying rate increased very rapidly with only a slight increase in rate of esterification.

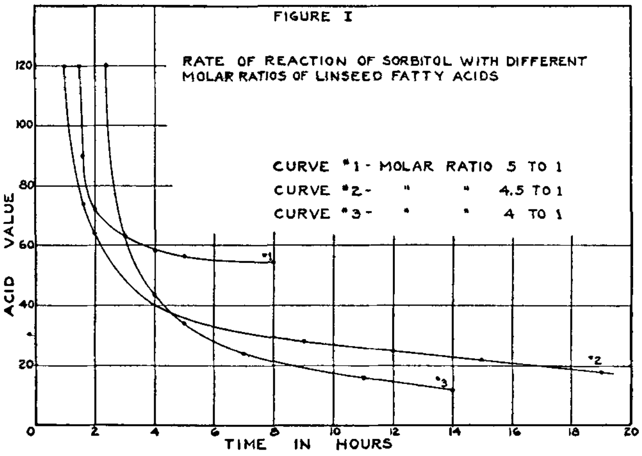

FIGURE I

RATE OF REACTION OF SORBITOL WITH DIFFERENT MOLAR RATIOS OF LINSEED FATTY ACIDS

Quite an extensive study of catalysts was made, but none was found that gave sufficiently good results to warrant its 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 number (2-5) was desired, the time necessary to arrive at this acid value was the same with or without catalyst.

The alkaline earths had, in general, the least effect on color for a corresponding increase in esterification rate. Acidic catalysts invariably gave a much darker colored product, camphor sulfonic acid being the least objectionable. If a lower temperature were used to overcome the loss in color, the small increase in initial esterification rate did not warrant its use.

The use of sulfur dioxide in place of an inert gas gives a product of improved color and materially increases initial esterification rate. However, SO_2 does not affect the final low acid number that can be reached in a given time; i.e. when SO_2 is used, the initial drop in acid value is very rapid but when the acid value reaches 15 or 20, the curve levels off. As much time is necessary to reach an acid value of 5 with catalyst as without.

To summarize—the best method of ester formation by reaction of polyhydric alcohol and fatty acids is as follows: Heat under vacuum, fatty acids and the theoretical amount, plus 5%, of alcohol at 450° F. SO_2, an inert gas, or steam is bubbled through rapidly to provide agitation and carry off water. The reaction vessel should be equipped with a condenser and an air-cooled reflux column to condense and return vaporized alcohols.

USING this method, a number of polyhydric esters of various fatty acids have been prepared in our laboratory. Following is a detailed description of the equipment and method: a 5-liter flask is fitted with three small side arms and a standard ground glass joint. In one side arm is inserted a thermometer, another provides a means for sampling the reaction mixture, and the third carries a tube through which inert gas or steam is blown to provide agitation and entrain water vapor. The main outlet is fitted with a vertical air condenser which in turn is connected to a water condenser, a receiving flask, a manometer, and a vacuum pump. All connections are standard ground glass joints. Heating is accomplished by means of a basket-type electric heater.

The flask is charged with fatty acids and the temperature raised rapidly to about 300° F. At this point the alcohol is added and the apparatus assembled and evacuated. Gas is bubbled rapidly through the reaction mixture to agitate it and to hold down foaming. The temperature is raised to 450° F. as rapidly as possible. If excessive foaming is encountered, the temperature is held down until the alcohol is in solution and foaming subsides. The reaction is then held at 450° F. throughout. Samples are taken periodically for acid number determination.

Using this general procedure, several experiments were conducted on the preparation of the sorbitol esters of linseed fatty acids (1). In the first runs the molar ratio of fatty acid to sorbitol was 5 to 1. At this ratio the acid number was found to decrease rapidly to about 60 in 4 hours and then leveled off and decreased very slowly on long continued esterification. The use of calcium oxide, (H_3BO_3) boric acid, and sulfur dioxide did not alter the results. With SO_2, however, the color of the final product was improved, 10 Gardner-Holdt as compared to 12-13 Gardner-Holdt without catalyst. The other catalysts actually caused a darkening in color.

Since it was obvious that this molar ratio would not give a good ester, the ratio was lowered to 4.5 to 1. In this run the initial drop to an acid value of about 40 was rapid (about 4 hours) and then again leveled off. No great decrease was noted in an additional 15 hours. Final acid value was 20.

In a third trial the molar ratio was decreased to 4 to 1. In 4 hours the acid value was 44; in 8 hours, 22; and in 14 hours, 14. After 20 hours of reaction an acid value of 10 is obtainable. This is sufficiently low for commercial purposes.

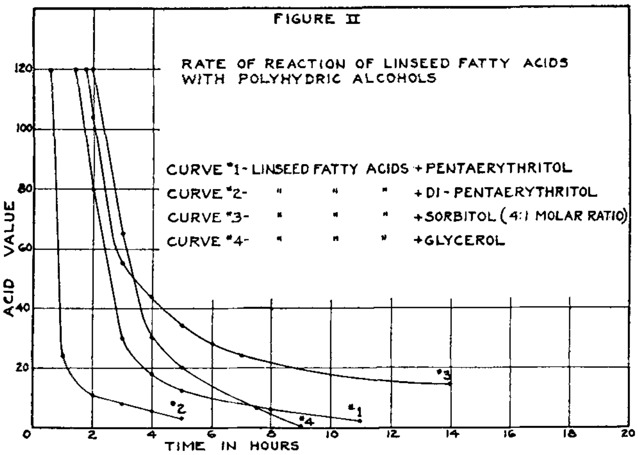

FIGURE II

RATE OF REACTION OF LINSEED FATTY ACIDS WITH POLYHYDRIC ALCOHOLS

These results are summarized in Figure I in which acid value is plotted against time of reaction for the three molar ratios. It is apparent from these curves that the initial reactions to an acid value of 60 during the first 3 hours are very similar; however, with a molar ratio of 5 to 1, the reaction practically stops at this point while with ratios of 4.5 to 1 and 4 to 1,

TABLE I.

Polyhydric Alcohol Esters of Linseed and Soybean Acids.*

Ester	Drying time (hours)	Sward hardness (time in hours)		
		24	48	120
Linseed–Glycerol	4	0	0	2
Linseed–Pentaerythritol	2.5	2	6	6
Linseed–Sorbitol	1.5	0	2	4
Soybean–Glycerol	....	0	0	0
Soybean–Pentaerythritol	3	2	2	4
Soybean–Sorbitol	3	2	2	2

*Archer-Daniels-Midland Co., "Water White Fatty Acids."

the curves level off at acid values of 40 and 20, respectively. Factors which undoubtedly prevent these reactions from going to completion are stearic hindrance, formation of inter-ethers and from a more practical standpoint, there is considerable charring and burning of the alcohol at the temperature required for esterification, 450° F.

Analysis upholds the premise that it is impossible to esterify all the OH groups in sorbitol with fatty acids since these esters had acetyl values in the neighborhood of 10 even after extended heating with excess acid. Very little heat polymerization of the oil occurred during esterification, final viscosity being 1.5 to 2 poises.

Continuing this work, linseed fatty acids were esterified with pentaerythritol, di-pentaerythritol, sorbitol and glycerol (3, 6). The same technique was used and results are summarized in Figure II. Stoichometric amounts of alcohol and acids were used in all esterifications except with sorbitol where the 4 to 1 ratio was used. The pentaerythritol reaction was difficult to handle due to vigorous foaming. This was overcome by holding the temperature at 350° F. for 2 hours until all alcohol was in solution. Very little distillation loss of alcohol occurred even with glycerol, due to the use of the air-cooled vertical condenser. Using stoichometric amounts of the reactants, an acid value of 1 to 2 was easily obtainable.

An examination of Figure II shows that the rate of esterification is directly controlled by the ratio of primary hydroxy groups to secondary hydroxy groups. Thus, di-pentaerythritol having the most primary groups gave the most rapid reaction, pentaerythritol having only primary (but fewer) groups was second, glycerol third, and sorbitol having a ratio of 1 primary to 2 secondary groups was the slowest.

The set-up time and hardness at various drying periods of these esters was studied. .2% Pb and .025% Co as metal was used as a siccative. Corresponding esters of soybean fatty acids were also examined in this series.

Results are tabulated in Table I.

This table indicates that set-up time is proportional to the number of hydroxyl groups in the alcohol (functionality) but the hardness is more directly related to the number of primary alcohol groups in the molecule. Other data which we are not at liberty to discuss also bears this out. Where varnishes are made from these esters, these relationships still hold.

The data also demonstrate the improvement in drying oils possible by replacement of glycerol with an alcohol of higher functionality. The improvement is especially marked in the case of the soybean esters which, although not approaching linseed esters in quality, have good enough drying properties to make them commercially valuable. The soybean esters show a greater improvement over the natural oil than do the linseed esters; however, the linseed esters set up faster and dry harder than the corresponding soybean esters.

As a final part of this work, pentaerythritol was esterified with linseed, soybean, castor,[2] high iodine value fish oil acids (220 I. V.)[3] and various mixtures of these fatty acids. A part of this data is given in Table II.

The conclusions to be drawn from these results are very general in that all the acids reacted very similarly with this alcohol to give an acid number around 5 in from 5 to 8 hours. Very little heat polymerization occurred as shown by the close proximity of final viscosities. The colors were all satisfactory with linseed being poorest and castor the best. All these esters dried rapidly to films of little tack and were very hard in comparison with natural glycerol ester.

The testing of these esters in varnishes is now going forward, but as yet not enough data are available for a comprehensive report. In general, the improved drying and hardness shown by the oils is carried over into the varnishes made from them. All of the synthetic esters show an improvement in bodying speed over the corresponding glycerol ester. In the same fashion improved water and alkali resistance is shown. The sorbitol esters do not show as much improvement as the pentaerythritol esters, however, and are definitely inferior to pentaerythritol esters in soap and alkali resistance. Di-pentaerythritol shows an advantage over pentaerythritol in hardness, mar resistance, and alkali resistance. All the synthetic ester varnishes have better abrasion resistance than corresponding glycerol ester varnishes.

There are two other polyhydric alcohols which we have examined but which we are not permitted to name. Both have more than six hydroxyls per molecule. Both esterify easily and give remarkable products. The linseed esters of these alcohols dry in 1 and 1½ hours, respectively, to a practically tack-free

TABLE II.

Preparation of Pentaerythritol Esters.

Fatty acids		Grams of alcohol	Hours at 450° F.	Acid No.	Viscosity (poises)	Color (G. H.)	Drying time (hours)
Type	Grams						
Linseed	2000	260	10	3.85	1.25	8-9	2.5
Soybean	2500	325	8.5	5.70	1.0	7	3
Castor	2500	325	5.0	1.50	2.1	5	2
High iodine fish oil acids (220 I. V.)	2500	325	6.0	4.93	2.4	6	1

---

[2] The Baker Castor Oil Company's "107 Acids—Distilled."

[3] The Werner G. Smith Company's "Hyodol Acids."

film. In varnishes both esters show properties closely akin to tung oil and, in fact, seem to have greater durability than tung oil varnishes upon exterior exposure. Perhaps at a later date we will be able to report in greater detail.

To summarize: optimum conditions for reaction of a fatty acid with a polyhydric alcohol to form an ester have been outlined; the value of catalysts has been found to be insignificant under these conditions. Some esters have been prepared and their properties discussed. From the qualities shown by these esters in varnishes it is felt that several of them are of value for the production of protective coatings. Blends of fatty acids to give certain definite properties to these synthetic esters will increase their value.

BIBLIOGRAPHY

1. Bouner, R. E., Brewster, M. D., MacGregor, W., Brauder, J. D., and Hunter, R. H.; Atlas Powder Company Bulletin, November 15, 1943.
2. Bradshaw, G. B., and Meuly, W. C. (to E. I. duPont de Nemours & Company) U. S. Patent 2,271,619 (February 3, 1942).
3. Burrell, Harry; Oil and Soap, *21*, 206-11 (1944).
4. Tsnchiya, T., and Ishikawa, T. J.; Soc. Chem. Ind., Japan *36*, 230-3 (1933).
5. Unpublished data.
6. Woodruff, H. C.; Paint, Oil and Chemical Review, *107*, 7 (1944).
7. Wright, H. J., Segur, J. B., Clark, H. V., Coburn, S. K., Langdon, E. E., and DuPuis, R. N.; Oil and Soap, *21*, 145-148 (1944).

Influence of pH of the Adsorbent on the Properties of Edible Oils and Fats

JOHN W. HASSLER
West Virginia Pulp and Paper Company
Tyrone, Pa.

IN THIS paper the phrase "pH of the adsorbent" refers to the pH of the water extract. Consequently, the numerical value depends on the conditions under which the extraction is conducted. In this work 1 gm. of adsorbent was stirred into 100 ml. distilled water, the mixture heated to 100°C., then cooled to room temperature, and the pH of the slurry determined electrometrically.

The pH of fuller's earth ranges from 7.0 to 10.0, depending on the source and the processing. Many active clays have a much lower pH ranging from 3.0 to 5.0, although a few are as high as 7.0. These activated clays are produced by the action of strong acids (HCl or H_2SO_4) on certain natural clays. The function of the acid is complex (1), some of it existing as an adsorbed layer or film.

The pH of a carbon may arise from various causes. Surface oxides (2) may be present, also, there is partial evidence that traces of some organic acids are formed during certain activation processes. Generally, however, the predominating factor is the effect of mineral constituents, some of which are derived from the original carbonaceous material whereas others are purposely added before activation to catalyze the development of certain adsorptive powers. Many of the mineral constituents undergo chemical change during the activation stage. In most processes the end products are alkaline resulting in the carbon exhibiting a pH from 8.0 to 11.0. However, in some processes the mineral constituents have final pH values as low as 3.0.

For some purposes the carbons are marketed without further processing but in many cases the pH is adjusted to a more neutral range by adding acid or alkali according to which may be required. In other cases the carbon is washed and in still others a combination of these treatments is employed.

When the adsorption of color is conducted from an aqueous solution the pH can have several effects, one of which is an indicator change. If we acidify an alkaline phenolphthalein solution, the pink color disappears. Similarly, if we add sufficient adsorbent of a low pH to an alkaline phenolphthalein solution the color will disappear from the filtrate but here we cannot know whether this is an indicator change or adsorption unless we apply a further test, e.g., add alkali to bring the filtrate back to the original pH.

Apart from any indicator influence, the pH of an adsorbent can have a marked influence on adsorption from aqueous solutions, especially when used in dosages sufficient to alter the pH of the solution. The degree of ionization or the chemical form of certain constituents may be altered so as to change the adsorbability, e.g., oxalic acid is strongly adsorbed by many carbons, whereas the adsorption of sodium oxalate is practically nil. Moreover, the solubility of many adsorbable substances is affected by pH conditions. Since the extent of an adsorption is a net effect of the relative attraction of the adsorbent as compared to the pull of the solvent, a change of solubility alters the extent of the adsorption.

THE influence of the pH of the adsorbent is not limited to aqueous solutions — for it has been found to affect adsorption from other solvents—sometimes with seeming inconsistencies. Thus, in adsorbing the dye, Ponceau 3R, a low pH carbon gave greater apparent adsorption from alcohol, whereas a high pH carbon was more effective for adsorbing this dye from pyridine. In contrast, a solution of Congo Red in pyridine was more effectively decolorized by a low pH carbon. These irregularities are only partially due to differences in adsorbability since color changes are also involved. The inconsistencies just quoted are purposely selected to show the complex factors that can exist.

However, reasonable consistency is found in very many cases—and this is true of the application of adsorbents to fats, oils, and waxes (3). There is rather consistent evidence that a high pH (above 9.5) is detrimental to color removal and sometimes this is true of pH values below 4. The reason for the detrimental influence of a high pH of an adsorbent is not clear but has been attributed to a catalytic action of certain alkaline chemicals in promoting oxidation. When the pH is low (particularly when