extent be independent of world supplies under emergency conditions. I believe the future of such research is virtually limitless.

In spite of the potentialities of fat interchangeability as indicated above, we must still consider the world fat situation as a whole in calculating our future course. What the future holds on the political and economic front is anyone's guess. The tense international situation has actually forced the nation to maintain a partial war economy. The stock piling of supplies and the subsidizing of planting of critical materials characteristic of our own economy are reflected on the whole world-wide front. When I asked my pet crystal ball what the drying oil situation would be next year, it grimaced and shuddered, and when I followed with a question as to what the world-wide fat situation would be in 1950, it groaned and broke into large and small pieces. If my crystal ball breaks down under such a simple question, who am I to try and give you the answer?

The Chemistry of Drying Oils

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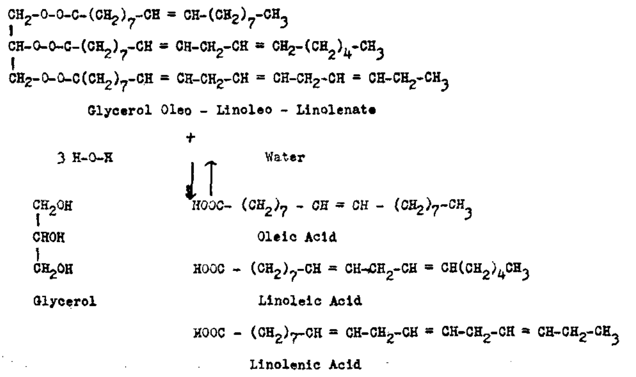
A DRYING oil is so-called because it dries, that is, it changes from an oily film to a tough insoluble film when exposed to air. This ability to polymerize by the action of the oxygen of the air is perhaps the most important chemical property of the drying oils (and the most difficult to completely explain chemically). Polymerization by heat is also important in making bodied oils for varnishes or for paints where the greater viscosity of the bodied oils controls penetration into porous surfaces. A discussion of the chemistry of the polymerization of drying oils by oxygen and heat will therefore be the principal object of this paper.

D. H. Wheeler

Other chemical properties of the drying oils and the drying oil acids are interesting as means of analysis, for making derivatives and modifications of the oils or acids. These chemical properties will also be discussed.

Drying oils, as they will be considered here, are the esters of naturally occurring unsaturated or drying fatty acids with polyhydric alcohols, or closely related compounds. Obviously then there are two parts to a drying oil, the unsaturated acid and the polyhydric alcohol.



These parts will be considered separately at first, and then the effect of their combination will be discussed with application of the concept of functionality to the drying and bodying properties of the drying oils.

The Unsaturated Acids

The unsaturated acids of greatest importance in drying oils are those containing 18 carbon atoms and two or more double bonds. These C_{18} polyethenoid acids occur as mixed glycerides in the common drying and semi-drying oils, such as linseed, perilla, tung, oiticica, dehydrated castor, safflower, soy, sunflower, corn, and cottonseed oils. The 20 and 22 carbon polyethenoid acids present in fish oils such as herring, menhaden, and sardine are also of considerable importance. In natural drying oils these acids always occur as mixed glycerides, esters of the trihydric alcohol, or glycerol.

Unsaturation of the polyethenoid acids may vary in two important respects:

1. The number of double bonds present.
2. The arrangement of the double bonds in relation to one another.

It is remarkable that the commercially important unsaturated acids have a double bond between carbon atoms 9 and 10, and no other double bonds closer to the carboxylic acid group.

Oleic acid has only one double bond and has very little activity as a drying oil component.

$$CH_3(CH_2)_7{-}CH{=}CH{-}(CH_2)_7{-}COOH$$

Oleic Acid

Linoleic acid has two double bonds separated by a methylene carbon atom and two single bonds.

$$CH_3(CH_2)_4CH{=}CH{-}CH_2{-}CH{=}CH{-}(CH_2)_7{-}COOH$$

Linoleic Acid

It is fairly active in its ability to polymerize by the action of oxygen or heat and is remarkable for its non-after-yellowing properties in alkyds and other protective coatings.

Linolenic acid, with three double bonds similarly separated, is much more rapid in its ability to polymerize by oxidation or heat.

$$CH_3CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CH(CH_2)_7{-}COOH$$

Linolenic Acid

It is the principal acid of linseed oil, the most important drying oil used in outside paints.

The C_{20} and C_{22} polyethenoid acids of fish oils are of similar general structure with two to five double bonds in the molecule. The double bonds in these acids are non-conjugated, in contrast to the conjugated double bonds in dehydrated castor, tung, and oiticica oils.

Conjugated linoleic acid occurs in dehydrated castor oil at about 25% (along with non-conjugated linoleic acid). The two double bonds, separated by one single bond, give the conjugated structure.

$$CH_3(CH_2)_5CH{=}CH{-}CH{=}CH{-}(CH_2)_7{-}COOH$$

Conjugated Linoleic Acid

This results in much greater speed in polymerization by oxygen or heat. Linoleic acid can also be conjugated by catalysts such as nickel or by alkali, but oils based upon such conjugated linoleic acid have not attained the commercial importance of dehydrated castor acids.

Eleostearic acid with three double bonds in conjugation is extremely rapid in its ability to polymerize by oxygen or heat.

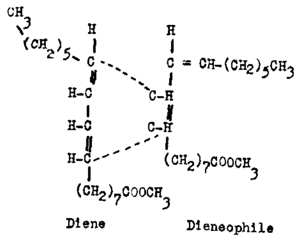
$$CH_3(CH_2)_3CH{=}CH{-}CH{=}CH{-}CH{=}CH(CH_2)_7{-}COOH$$

Eleostearic Acid

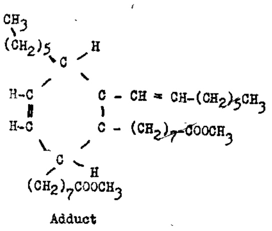
Hence tung oil is about the fastest drying and heat polymerizing oil known. Unless special steps are taken, the rapid surface drying and shrinkage of tung oil films results in wrinkled surfaces, which is desirable in some special finishes. Licanic acid in oiticica oil is similar to eleostearic but has a keto group on carbon atom 4.

The two most important properties of the multiple double bonds of these polyunsaturated acids are their ability to polymerize by the action of oxygen and to polymerize by the action of heat. There is a remarkable similarity in the relative speed and the degree of polymerization of the esters of the polyethenoid acids whether caused by heat or by oxygen. The mechanism of polymerization by the two agents is quite different however.

Thermal Polymerization. The polyethenoid acids or their alkyl esters combine with one another when heated. Two, and sometimes three, molecules are combined chemically through carbon-to-carbon bonds to form dimers or trimers. If the polyethenoid ester is conjugated, the dimerization reaction is believed to be a Diels-Alder addition reaction, with one molecule functioning as dieneophile and the other molecule functioning as diene.



Conjugated Linoleate; 9,11



A Dimer of Linoleate

Trimer may be formed by a double bond of the dimer acting as dieneophile, and another molecule of conjugated ester acting as diene.

If the polyethenoid ester is non-conjugated, it is believed that it shifts to the conjugated structure by the action of heat.

$$CH_3(CH_2)_4{-}CH = CH{-}CH_2{-}CH = CH{-}(CH_2)_7 - COOCH_3 \xrightarrow[\text{catalyst}]{\text{heat or}}$$

Normal Linoleate; 9, 12.

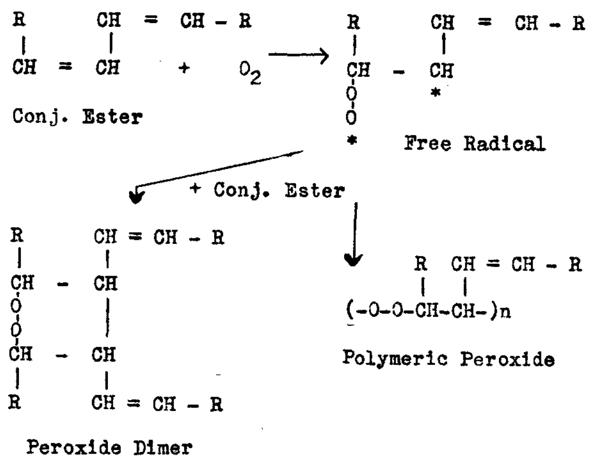
$$CH_3(CH_2)_5{-}CH = CH{-}CH = CH{-}(CH_2)_7 - COOCH_2 \xrightarrow{\text{heat}} \text{Dimer}$$

Conjugated Linoleate; 9,11 (or 10, 12)

This conjugated ester then acts as the diene, adding to the double bond of another conjugated or non-conjugated ester which acts as dieneophile, to form a dimer similar to that resulting when conjugated ester is the starting material.

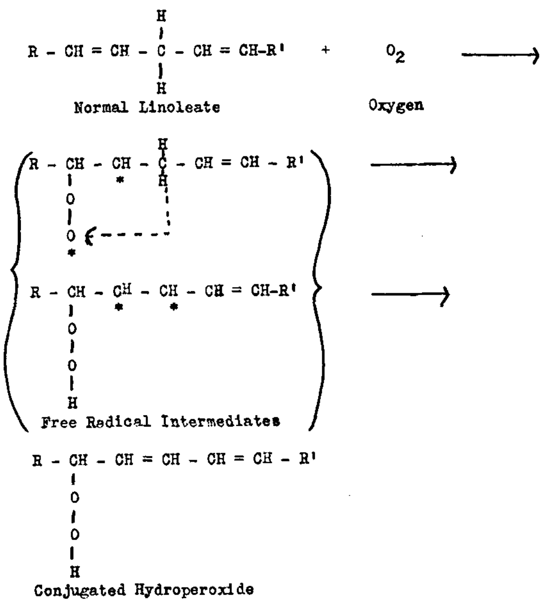
Shift of the non-conjugated form to the conjugated form is relatively slow and accounts for the slower rate of heat polymerization of the non-conjugated esters. The faster rate of the trienes compared to the dienes may be explained by the greater concentration of double bonds which can undergo reaction to conjugate and add to form dimer.

Oxidative Polymerization. The polyethenoid esters combine with one another when subjected to oxidation by oxygen of the air. This reaction is involved in the preparation of blown oils and in the drying of paint films. The reactions involved in oxidative polymerization are much more obscure and complicated than those in thermal polymerization. The increase in saponification value of oxidized esters indicates that new ester groups are formed which may link molecules together. There are some indications that ether linkages are formed by the combined oxygen, linking two molecules together. Conjugated esters generally react with oxygen and polymerize more rapidly than non-conjugated esters and require less oxygen to cause their polymerization. They do not form hydroperoxides to the extent that the non-conjugated esters do. The reactions involved are not clearly understood. Polymeric peroxides with peroxide groups joining two molecules are a possibility as well as carbon-to-carbon linkages.



The structures shown are speculative and not definitely known.

Non-conjugated esters are now known to form hydroperoxides with a shift of the double bond resulting in conjugated hydroperoxides.



The conjugated ester thus formed may then oxidize by the rapid (but unknown) mechanism by which the conjugated esters polymerize with oxygen. This shift to the conjugated form by the action of oxygen is qualitatively similar to the thermal conjugation mechanism described above.

Free radicals may be formed as intermediates in the hydroperoxide formation, and the hydroperoxides may decompose to give free radicals. These free radicals may combine to join two molecules by carbon-to-carbon or by carbon-to-oxygen to carbon bonds.

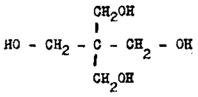
It is obvious from what has just been said that the reactions involved in oxidative polymerization are quite complex and not definitely known. Although this mechanism of oxidative polymerization is not definitely known, it is known that the oxidative polymers of the alkyl esters of these unsaturated acids are mostly dimers with perhaps some trimers or higher polymers. Thus the similarities between oxidative and thermal polymerization are:

1. Mostly dimers, some trimers, but probably nothing much higher than trimers are formed from alkyl mono-esters.
2. Shift of the non-conjugated to the conjugated form occurs in both cases and is probably an important step in the mechanism in both cases.
3. The relative speeds of polymerization of the various polyene acid esters are similar by both methods of polymerization, with few exceptions.

Polyhydric Alcohols

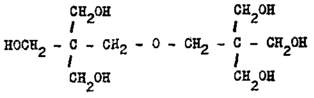
The trihydroxy or trihydric alcohol, glycerol, is the alcohol with which the drying acids occur combined as glycerides in natural oils. With three hydroxyls it can combine with three fatty acids to give triglycerides. For reasons which will be seen later it is often desirable to combine more than three fatty acids in a drying oil molecule, and numerous chemical means have been devised to accomplish this.

Pentaerythritol with four hydroxyls is the most important synthetic polyhydric alcohol used with drying acids to make drying oils and resins. Dipentaerythritol with six hydroxyls is also formed when pentaerythritol is manufactured.



$HO-CH_2-C(CH_2OH)_2-CH_2-OH$

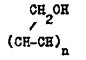
Pentaerythritol



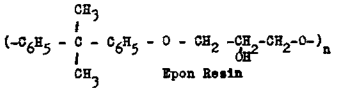
$HOCH_2-C(CH_2OH)_2-CH_2-O-CH_2-C(CH_2OH)_2-CH_2OH$

Dipentaerythritol

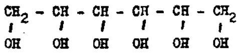
Other polyhydric alcohols which have been used to a lesser extent include polyallyl alcohol, the Epon resins, sorbitol, manitol, and tetramethylol cyclohexanol.



Polyallyl Alcohol

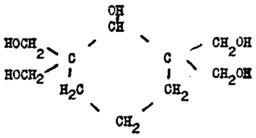


Epon Resin



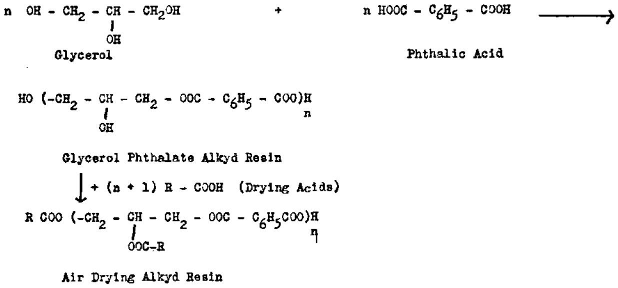
$CH_2(OH)-CH(OH)-CH(OH)-CH(OH)-CH(OH)-CH_2(OH)$

Sorbitol or Manitol



2,2,6,6 - Tetramethylolcyclohexanol

Alkyd resins can be considered as fatty acid esters of a special kind of polyhydric alcohol. If a dibasic acid such as phthalic acid is reacted with the trihydric alcohol glycerol, mole for mole, a polyester resin may be formed which has a number of left-over hydroxyl groups which are free to be esterified with fatty acids.



If pentaerythritol is used instead of glycerol, more free hydroxyl groups are left, and more fatty acids can be combined into the molecule of alkyd resin. Actually one does not usually react the polyhydric alcohol and dibasic acid first and then esterify with fatty acids, as implied. Frequently all reactants are added at once, or the partial ester of the fatty acid and polyhydric alcohol is first formed and then reacted with the dibasic acid. However the result is qualitatively similar.

Functionality in Drying Oils

Functionality is the measure of the ability of a compound to chemically combine with another compound. Drying acids have two types of functionality:

1. The functionality of the carboxyl group.
2. The functionality of the double bonds.

It is important to realize that these two types of functionality are usually exerted under different conditions.

Carboxylic acid functionality is exerted when a fatty acid reacts to form an ester with a hydroxyl group. Thus fatty acids with one carboxyl group have a functionality of one as far as ester formation is concerned. When the carboxyl group is esterified, it no longer has any functionality. The alcohols are the complementary functional groups to the carboxylic acid groups. Glycerol, with three hydroxyls, has a condensation functionality of three for combining with carboxyl groups, pentaerythritol four, dipentaerythritol six, and so on.

Thus the carboxyl group has the important function of affording a means of attaching fatty acids to polyhydric alcohols so that the resulting drying oil or resin may further polymerize by means of the multiple double bond functionality thus introduced.

Double bond functionality is exerted when a drying oil or resin is heated to body it or when it is spread in a film to dry by oxidation. For purposes of discussion in this paper double bond functionality will be limited to the ability of the double bond systems of an unsaturated acid ester to unite chemically with another unsaturated ester under the action of oxygen or heat. As may be seen, the chemical mechanisms of heat polymerization and of oxidative polymerization are quite different, but in each case the principal product is a dimer when an ester of a monohydric alcohol is the starting material. This means that the double bond functionality of these drying acid esters is approximately one, that is, it can combine with one other drying acid ester. (The average double bond functionality of linolenic and eleostearic acid monoester may be somewhat greater than one, but it is not more than two.)

High polymer formation is related to functionality in a definite way. The formation from drying oils of paints and varnishes which will dry to tough, hard protective films depends upon their ability to form high polymers. In a mono-functional system the monomer has a functionality of one; it can form only a dimer with another molecule of monomer. This is essentially the case with methyl esters of drying acids since only one drying acid is present per molecule.

In a bifunctional system the monomer has a functionality of two; and high molecular weight polymers may be formed, theoretically infinite molecular weight at complete reaction. This is because of the fact that when two such monomers combine to form a dimer, the functionality of each monomer is reduced by only one so the resulting dimer still has a functionality of two. It can then react with another monomer (or dimer) to make a trimer (or tetramer), which still has a functionality of two. The reaction can thus continue to very high polymers. At any reasonable degree of reaction the average molecular weight may be high but finite (depending on the degree of reaction), and the polymer is usually soluble and fusible.

In a trifunctional system, when the trifunctional monomer combines with another trifunctional monomer, it gives a dimer which has a functionality of four since only one functional group is used in each monomer to form the dimer. As each trifunctional monomer adds to the polymer, the functionality of the polymer is increased by two. It is obvious that extremely high polymers can result, even at a relatively low degree of reaction. If the degree of reaction is great enough and the polymers are so large that they are insoluble and infusible, they are said to be gelled. By a similar line of reasoning any monomer with an average functionality greater than two will be seen to be capable of gellation since the functionality of the polymer is increased by every addition of monomer. The greater the functionality, the greater is the average molecular weight and tendency to form extensive gels of "infinite" molecular weight at a given degree of reaction. It is the formation of these polymers of high molecular weight which is largely responsible for the formation from drying oils and resins of tough durable films which are resistant to water, chemicals, and solvents.

With these semi-quantitative relationships of functionality to polymer formation and a consideration of the relative speeds of reaction of double bond systems previously discussed, a qualitative explanation of the drying and heat bodying properties of drying oils and resins is possible.

It is obvious that for a given polyhydric alcohol ester the greater the percentage of drying acids, the greater the average double bond functionality of the ester "monomer." For instance, a fatty acid with a double bond functionality of one, when esterified with glycerol, gives a triglyceride with a double bond functionality of three. If only two-thirds of the fatty acids are monofunctional, the average functionality of the triglyceride is two. Thus tung oil, a triglyceride with 80% of its acids being the very rapidly reacting conjugated eleostearic acid, polymerizes extremely rapidly by heat or oxygen. Linseed and perilla glyceride oils with about 70% drying acids (mostly the rapidly reacting linolenic acid) are fast drying and bodying oils. Safflower oil with 70% of the slower reacting linoleic acid is slower drying than linseed but still a fairly fast drying oil. Soybean oil with only 60% of drying acids, mostly linoleic, dries very slowly and incompletely and heat bodies relatively slowly. Corn and cottonseed oils, with only 45-50% of linoleic acid, are classed as non-drying oils.

For a given percentage of drying acids the average double bond functionality will be greater, the greater the number of hydroxyl groups of the polyhydric alcohol which are esterified with fatty acids. For instance, the glyceride of a fatty acid mixture which is two-thirds acids with a double bond functionality of one would have an average double bond functionality of two whereas the dipentaerythritol ester would have an average functionality of four and the pentaerythritol ester an average functionality of two and two-thirds. Thus the pentaerythritol ester of soya acids approaches linseed oil in drying properties and has been used as a partial replacement for linseed oil. Drying alkyds, esters of the Epon resins and of polyallyl alcohol, have in each molecule a still larger number of alcohol groups esterified with fatty acids. The double bond functionality is thus increased so much that such esters made with soybean or fractionated cottonseed acids have excellent drying properties. In such resinous drying esters, the ester ("monomer") is already of considerable molecular weight. This fact, combined with the hardening effect of the resin structure and with the high double bond functionality, confers to the paints made from drying alkyds the unusually rapid drying and excellent durability which have resulted in their recent phenomenal growth.

In these drying alkyds there is often a certain advantage in using the more slowly polymerizing linoleic-rich acids, compared to the faster linolenic acids of linseed or perilla oils. Alkyds made from acids containing little or no linolenic acid produce films which develop little or no after-yellowing upon aging of the paint. They are therefore used widely in white and light-colored interior finishes. Greatest speed in drying without after-yellowing is obtained by the use of soybean or cottonseed acids which have been enriched in linoleic acid by removal of saturated acids. This removal is accomplished commercially by fractional distillation or crystallization.

The chemistry of the drying and polymerizing properties of drying oils and resins may then be briefly summarized as follows:

1. The relative speed of polymerization by oxygen and by heat is similar for the esters of the various unsaturated acids.
2. Polymerization rate of esters of drying acids is increased by increase in the number of double bonds in the drying acids.
3. Conjugated unsaturation causes more rapid polymerization than non-conjugated unsaturation.
4. The carboxylic acid functionality of drying acids is essential in that it is the means of attaching them to polyhydric alcohols by esterification so that a number of drying acids can be attached to a drying oil or resin molecule. The carboxylic acid functionality is then used up.
5. The double bond functionality of the drying acid esters is responsible for their polymerization by oxygen (drying) or by heat (heat bodying).
6. The double bond functionality of the various individual drying acids is approximately one (at least probably not more than two), but it is additive when a number of drying acids are combined by esterifying them with a polyhydric alcohol. The drying oils and resins ("monomers") thus formed may then have an average double bond functionality greater than two.
7. The greater the double bond functionality of a drying oil or resin, the faster and more complete will be its polymerization by oxygen or heat.
8. Double bond functionality may be increased in a drying oil or resin by two means:
    a) Increasing the number of drying acids in each molecule of oil or resin by increasing the number of hydroxyl groups which are esterified by fatty acids.
    b) Increasing the percentage of drying acids in the fatty acids used to esterify the hydroxyl groups.
9. The rate of polymerization of a drying oil or resin by oxygen (drying) or by heat (heat bodying) will depend on two principal factors.
    a) The average double bond functionality of the ester.
    b) The inherent speed of polymerization of the individual drying acids which are responsible for the double bond functionality.
10. Drying alkyd resins give excellent film properties because of a combination of factors:
    a) High double bond functionality is present due to the presence of many drying acids per molecule.
    b) The phthalate resin structure contributes a hardening effect.
    c) The "monomer" molecule is already built up to a relatively large size so that further polymerization by double bond functionality rapidly results in polymerization to a highly gelled film.

Other Reactions of Drying Oils and Drying Acids

The double bonds of the drying oil acids show the many reactions characteristic of double bonds in any other organic chemical.

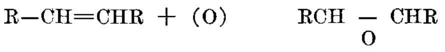
Hydrogen adds on to saturate the double bond. Oleic acid adds one mole (two atoms) of hydrogen to produce stearic acid. Linoleic acid adds one mole of hydrogen to give oleic acid (or an isomer) and then another mole to produce stearic acid. The other polyene acids similarly add hydrogen eventually to give saturated acids. The partially hydrogenated semi-drying and non-drying oils are important as vegetable shortenings.

The halogens (chlorine, bromine, iodine) add to the double bonds of the unsaturated acids. Quantitative determination of the amount of halogen added is the basis of determining the amount of total unsaturation in an unsaturated acid or oil. The iodine value is calculated as the number of grams of iodine which is absorbed by 100 grams of material. Conjugated unsaturation does not add halogen completely unless special conditions of reagent or catalyst are employed. Thiocyanogen $(SCN)_2$ adds to double bonds. It adds quantitatively to the double bond of oleic acid. It adds to only one of the two double bonds (approximately) of linoleic acid and to two of the three double bonds (approximately) of linolenic acid. By determining the thiocyanogen absorption value and the iodine value of mixtures of oleic and linoleic and saturated acids, the composition can be determined. In a mixture of oleic, linoleic, linolenic, and saturated acids, it is necessary to determine the percentage of saturated acids as well as the thiocyanogen and iodine number in order to determine the composition.

The bromine addition products of linoleic and linolenic acids are of interest as means of qualitatively and quantitatively identifying these acids. Linoleic acid adds four atoms of bromine to give a crystalline tetrabromostearic acid (m.p. 115.5°C.) in about 50% yield. By determining the yield under definite conditions, the percentage of linoleic acid may be estimated. By removing the bromine from the pure tetrabromide with zinc, a linoleic acid is regenerated which is quite pure.

Linolenic acid similarly adds 6 atoms of bromine to afford a crystalline hexabromide (m.p. 180°C.), which can similarly be made the basis of a quantitative estimation and can be debrominated to produce linolenic acid.

Addition of oxygen to a double bond by peracids such as peracetic or perbenzoic acid produces the epoxide group:



$$R{-}CH{=}CHR + (O) \qquad \underset{O}{RCH - CHR}$$

The epoxides can react with water to form dihydroxy compounds; with alcohols to form hydroxy ethers; with carboxylic acids to form hydroxy esters, or with hydrochloric acid to produce chlorohydrins. The reaction with hydrochloric acid is the basis of a method of determining epoxy groups, by measuring the amount of hydrochloric acid consumed in the reaction.

Double bonds may be hydroxylated to attach two hydroxyl groups which saturate the double bond. By reaction with dilute alkaline permanganate, oleic acid affords 9,10-dihydroxy stearic acid, m.p. 132°C., whereas reaction with peracetic acid, followed by hydrolysis, produces an isomeric 9,10-dihydroxy stearic acid, m.p. 95°C. Linoleic acid produces two isomeric 9,10,12,13-tetrahydroxy stearic acids, m.p.'s 163.5° and 174° when hydroxylated by permanganate. Linolenic produces two isomeric 9,10,12,13,15,16-hexahydroxy acids, m.p.'s 173° and 203°.

Maleic anhydride adds to unsaturated acids or esters. Conjugated unsaturated acids add maleic anhydride by the Diels-Alder reaction at fairly low temperatures. This reaction is the basis of several methods for determining conjugation in oils such as tung and dehydrated castor. At higher temperatures the non-conjugated acids or esters also react with maleic anhydride by a different mechanism. Oleate adds one mole of anhydride slowly to produce a substituted succinic anhydride which still has one double bond. With excess anhydride, linoleate adds two moles and linolenate adds nearly three moles of anhydride. When an excess of anhydride is not used, there is evidence that three moles of linoleate may be joined together by two moles of anhydride. In any case the carboxylic anhydride group of the maleic anhydride is still present in these adducts with unsaturated fatty esters. The maleic anhydride treated oils can therefore be reacted with polyhydric alcohols to produce polymeric oils of enhanced drying properties.

Styrene can add onto unsaturated fatty acids or esters under certain conditions of heat and catalysis. Conjugated unsaturation is apparently necessary or desirable for this reaction. Although the exact mechanism is not known, the general result is the attachment of a polystyrene resin residue to the unsaturated ester. The resulting styrenated oils and alkyds have good water and alkali resistance and are being produced commercially.

A double bond in an unsaturated acid can exist as two geometric forms, the cis and trans forms. The naturally occurring oleic, linoleic, and linolenic acids are all in the cis form. The cis form can be converted to the trans form by the catalytic action of selenium at 200°C. or by the action of the oxides of nitrogen. The trans forms are generally higher melting than the cis forms and are more stable to oxidation. In ordinary processing for the production of drying oils and fatty acids there is apparently no conversion of the naturally occurring cis to the trans form. Some formation of the trans form does occur during hydrogenation.

Ultraviolet absorption is a new, valuable tool in the analysis of drying oils and acids. The non-conjugated acids absorb very little in the near ultraviolet whereas the conjugated acids have strong absorption bands. Conjugated diene absorbs at about 2300Å, but very little at 2700Å. Conjugated triene absorbs at about 2700Å, but very little at 2300Å. It is therefore possible to analyze for conjugated dienes and trienes in a mixture of either or both in non-conjugated acids or esters. When normal linoleate is treated in alkaline solutions at a high temperature under definite conditions, it is converted extensively and reproducibly to a conjugated linoleate, and the increase in absorption at 2300Å of the alkali isomerized linoleic acid is a measure of the amount of the original normal linoleic acid. When normal linolenate is similarly isomerized, it develops both conjugated diene and conjugated triene in a reproducible ratio. The increase in absorption at 2700Å of the alkali isomerized acids is a measure of the amount of original normal linolenic acid. The fact that linolenic acid also forms conjugated diene necessitates a correction for its absorption at 2300Å, when linoleic acid is determined in the presence of linolenic acid. The whole method is relatively simple and rapid, requires only a small sample, and is generally the most satisfactory method of analysis of the drying acids or their esters.

Carboxylic acid reactions of the drying oil acids are those to be expected of any carboxylic acid. Esterification is the most important reaction in drying oils and resins as discussed above. The methyl esters are often used for fractional distillation to analyze for chain length. The C_{18} unsaturated acids or methyl esters cannot be separated to any practical degree by fractional distillation however. The other usual reactions of carboxylic acids are shown by the unsaturated acids: formation of acid chloride, amide, nitrile, and amine by the usual methods. Salts of alkali metals are readily formed from the oil or acid and the alkali metal hydroxide. The potassium soaps are used as liquid and gel scrub soaps. The manganese and cobalt salts are used to a limited extent as driers. They are made by reacting a solution of the sodium or potassium soap with a soluble cobalt or manganese salt.

In summary, chemical reactions of the unsaturated fatty acids or esters are thus seen to be essentially those to be expected from their structure: esterification, salt formation, and the other usual reactions of the carboxylic acid group and additions at the double bond.