started us along this road and progress should be rapid from now on. There is and will be a need for extremely fast drying oils in the printing ink and protective coatings industry. Tung oil is now the criterion but in the future it probably will be judged a comparatively slow oil. For printing inks a "flash" dry is becoming almost a necessity, and future requirements of mass production industries will demand faster hardening coatings than are now available.

6. Copolymers of drying oils with monomers such as styrene, methyl methacrylate, etc. Several patents have been issued on such products and the possibility of valuable developments along this line seems assured.

7. To accomplish the above-mentioned objectives I believe that several fundamental studies must be undertaken and successfully concluded. I shall list these as follows:

a. Further study of the configuration of fat acid molecules and the characteristics of the various isomers of each acid. Perhaps this study will demonstrate why two oils of the same Iodine value have greatly different polymerization rates, a problem which frequently arises. An elaidinization process might be used to improve either the oxidation or polymerization qualities of an oil.

b. Further development of the spectrograph and other analytical tools for work with oils and fat acids.

c. A cheap, efficient and controlled method of isomerization of nonconjugated acids and oils to the conjugated form.

d. A cheap, efficient and controlled method of hydroxylation of unsaturated oils or acids. This I believe to be of great importance. Hydroxy acids now have a large usage in plasticizers and surface active agents. Both fields will develop greatly in the future and more hydroxy acids will be needed.

Besides this ready-made market hydroxy acids are valuable as intermediates. For example, the hydroxy acids are split at the OH group to produce dibasic acids. By controlling the position of the hydroxyl group a great variety of useful dibasic acids could be made.

By hydroxylation and dehydration a great variety of highly unsaturated acids could be made.

e. Another method of accomplishing the same thing would be catalytic hydration of fat acids.

f. Further methods of production of highly unsaturated fat acids suggest themselves. This might be accomplished by halogenation and dehalogenation; by hydrohalogenation and dehydrohalogenation (both unsuccessful so far) or by catalytic dehydrogenation. The latter is well known in the petroleum industry but low temperature processes for use with fat acids have not been developed as yet.

g. A corollary is the thorough study of addition of various groups at fat acid double bonds and subsequent removal or reaction of the added group.

h. Esterification of fat acids with extremely reactive alcohols and the study of polymers obtained from such esters.

i. Further work on polyamides of fat acids.

j. A method of introducing a carboxyl group into the carbon chain to form poly basic acids.

The absolute prerequisite to successful commercial application of anything discussed so far is an efficient, practical method of separating fat acids. When this is accomplished, we shall have in fatty oils, both drying and non-drying, a great and inexhaustible source of high molecular weight aliphatic compounds. These compounds can well be the basis for a new and great chemical industry. Such an industry would be of inestimable value to the United States for it would help provide a solid foundation for America's greatest industry, agriculture.

Some Known Reactions of Drying Oil Films and Polymerization

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Drying

DRYING OILS consist of esters of glycerol and organic long chain saturated and unsaturated aliphatic acids. Possessing the property to form solid films, they are the basis of air drying paints, varnishes, lacquers, linoleum and allied industries. The most widely used drying oil is linseed oil. The following is a percentage analysis of a Bison sample of linseed oil quoted by Jamieson: oleic acid 28.10%, linoleic 23.10%, linolenic 32.70%, palmitic 5.94%, stearic 4.00%, arachidic 0.30%, and lignoceric 0.21%. Linolenic and linoleic acids which impart the drying qualities to linseed oil have their unsaturated linkages separated from one another by saturated linkages; in elaeostearic acid, which is an isomer of linolenic acid, the linkages are conjugated.

Linolenic Acid:

$$CH_3CH_2CH{:}CH\cdot CH_2CH{:}CH\cdot CH_2CH{:}CH(CH_2)_7COOH$$

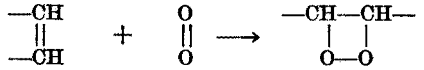
Elaeostearic Acid:

$$CH_3CH_2CH{:}CH\cdot CH{:}CH\cdot CH{:}CH(CH_2)_7COOH$$

The conjugated elaeostearic acid ester in tung oil imparts to it the excellent drying and polymerization qualities, resulting in the highly valued properties of its films.

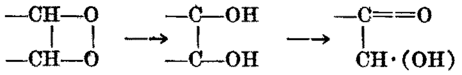
So far, no positive hypothesis relating to the mechanism of drying oils has been established. However, observation of the chemical and colloidal changes taking place during the drying is being accumulated and interpreted, with good promise of clarification of the problem. The purpose of this paper is to describe some of the reactions which have been rather well established by various investigators.

It is now fairly certain that the first chemical reaction during the drying of the film is the formation of a peroxide:



$$\begin{array}{c}\mathrm{-CH}\\ \|\\ \mathrm{-CH}\end{array} + \begin{array}{c}\mathrm{O}\\ \|\\ \mathrm{O}\end{array} \longrightarrow \begin{array}{c}\mathrm{-CH-CH-}\\ |\qquad|\\ \mathrm{O-O}\end{array}$$

It has also been ascertained that the peroxide rearranges itself into the following groupings:



$$\begin{array}{c}\mathrm{-CH-O}\\ |\qquad|\\ \mathrm{-CH-O}\end{array} \longrightarrow \begin{array}{c}\mathrm{-C-OH}\\ |\\ \mathrm{-C-OH}\end{array} \longrightarrow \begin{array}{l}\mathrm{-C{=}O}\\ \ |\\ \mathrm{CH\cdot(OH)}\end{array}$$

The presence of peroxides in ever-increasing quantities during the drying of films, in linoxyn as well as in air-oxidized oils in general, has positively been established. The formation of hydroxyl groups is evident from the increased acetyl value of the drying film. The assumption that poly-ketones are formed during drying in the dark is supported by the fact of the yellowing of films. It is known that diketostearic acid has a yellow color and ketohydroxystearic acid is colorless.

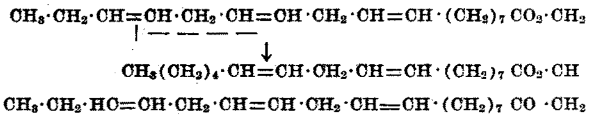
During the induction period the weight of drying films increases very slowly, but after a certain interval it becomes rapid until a maximum is reached and then the weight decreases. The changes in weight are due to a combination of oxygen absorption and losses caused by volatile gases as by-products of oxidation. The amount of oxygen absorbed by linseed oil during drying is higher than the increase of weight of the film—the difference obviously is due to volatile byproducts. The changes of weight vary with the chemical structure of the drying oils. Oils with high contents of linoleic acid suffer higher losses than those in which linolenic acid predominates. After the induction period the films acquire a strong peroxide reaction, and it is assumed that these peroxides serve as catalytic accelerators of further oxidation, promoting molecular reorientation required to cause gelation of the film. This view is supported by the fact that in the presence of catalytic driers the induction period is either entirely eliminated or considerably shortened.

The drying progress of a film depends on the nature of the fatty acids and the size of the ester molecule. It is known that neither fatty acids nor their mono-alcoholic esters will gel but acquire this property in proportion to the basicity of the esterifying alcohol. From this it is evident that the ester molecule must contain a sufficient number of reactive points to be able to form a complex compound with potential colloidal properties to gel. Once the film has absorbed the maximum amount of oxygen, gelation occurs without chemical changes, this being the phase when colloidal forces set in. Indications are that adsorption of the liquid by the gel causes a gradual reduction of the liquid phase, thus forming the final film, and that the hardening of the film consists in a gradual transition of the oxidized compounds to a solid phase of substantially the same composition.

However incompletely, this brief outline indicates the course of drying oil reactions: (1) the formation of peroxides as the primary reaction; (2) the rearrangement of the peroxides into hydroxylated ketonic forms; (3) molecular weight of films indicates the formation of monomers. The drying progress proceeds in various stages: (1) slow induction period; (2) followed by rapid oxidation; (3) maximum oxidation; (4) formation of gel consisting of infusible polymers. Films of various oils require different times to become infusible; poppyseed oil films remain indefinitely fusible; linseed and Chinawood oil films become infusible in from two to three weeks; films from all polymerized oils become infusible in a much shorter time. According to Bradley, infusible and insoluble polymers are of the cross-linked or three-dimensional form. Hence the formation of an infusible and insoluble film constitutes a conversion of a lineal to a three-dimensional form. Therefore, according to this theory, the primary prerequisite of a drying oil would be the possession of a structure which will form a three-dimensional polymer. Another very interesting theory (Blom) assumes that the primary oxidation products associate to form molecular complexes which are driven to the surface by the Gibbs-Thompson pressure which act as nuclei for the growth of higher polymers. Tackiness is the first evidence of this change, resulting in the formation of a skin by compression of solvate sheaths. Network development proceeds inward and aggregation is promoted by Van der Waal's forces.

Polymerization

DRYING OILS heated either in the open air or under vacuum acquire an increasing viscosity, a procedure known as polymerization. Linseed oil when so heated shows a rapid decrease of the hexabromide and iodine values and a rise of the refractive index. During the first stage while the iodine and hexabromide values decrease, there is hardly any increase of viscosity or molecular weight. This could be explained by assuming that the first reaction is of an intermolecular nature where there would naturally be no change in molecular weight: a glycerol ester of linolenic and linoleic acids could accordingly react as follows:



$$\begin{array}{l}\mathrm{CH_3{\cdot}CH_2{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH{=}CH{\cdot}(CH_2)_7\,CO_2{\cdot}CH_2}\\ \qquad\qquad\qquad\qquad\downarrow\\ \qquad\qquad\mathrm{CH_3(CH_2)_4{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH{=}CH{\cdot}(CH_2)_7\,CO_2{\cdot}CH}\\ \mathrm{CH_3{\cdot}CH_2{\cdot}HO{=}CH{\cdot}CH_2{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH{=}CH{\cdot}(CH_2)_7\,CO\,{\cdot}CH_2}\end{array}$$

Polymerization does not seem to set in until the iodine value has become more or less constant. As the molecular weight increases the oil becomes less soluble in acetone. As in drying, the nature of the alcoholic group plays an important role in polymerization. This is evident from the fact that monoesters of elaeostearic acid do not gel, whereas the glycerol esters will do so almost spontaneously. Evidently the number of active acids in the proximity of the molecule are of great influence.

Distillation of the ethyl esters of the acids of polymerized oil at various stages shows a gradual increase of molecular weight and also the very interesting fact that only a certain amount will distill under vacuum: the non-distillable part is assumed to be completely polymerized. Taken in conjunction with Long's work on blown oils, this suggests that a gel structure is formed by a small portion of the oil becoming highly polymerized and enmeshing or adsorbing the unpolymerized material. The theory of colloidal formations is strengthened by the fact that increase of viscosity does not occur until the refractive index and bromine value become constant, and that up to the point preceding gelation the molecular weight of the polymers does not exceed the dimeric form.

The above observations enable a partial visualization of the mechanism of drying oil polymerization.

(1) Polymerization is preceded by isomerization of the unsaturated acids containing two or three double bonds resulting in a conjugated system. This theory is supported by direct analytical methods and also by the fact that triolein, which is unable to form a conjugated system, cannot be polymerized.

(2) The conjugated systems build larger molecules until a semi-rigid structure is reached, resulting in gelation.

(3) Tung oil already containing a conjugated system is capable of almost instantaneous polymerization, while nonconjugated oils first must undergo isomerization, and hence the much slower progress of polymerization.

(4) When the required amount and proper size of molecules are built, colloidal forces cause gelation.

Pentaerythritol Drying Oils

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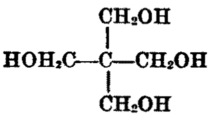
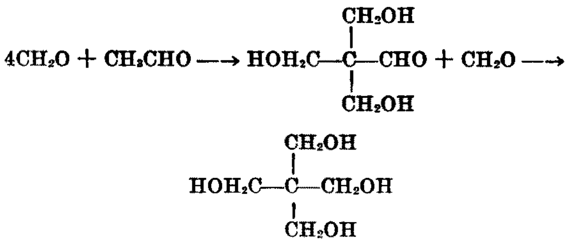
Pentaerythritol (tetramethylolmethane) the preparation of which was reported in 1891 by Tollens and Wigand (12) is a tetrahydric, primary alcohol having a quartenary carbon atom and the structure



$$\begin{array}{c} \mathrm{CH_2OH} \\ | \\ \mathrm{HOH_2C{-}C{-}CH_2OH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

The name pentaerythritol is an unfortunate misnomer since it is not accurately descriptive and is also difficult to pronounce; nevertheless, the usage is firmly established and it seems best to retain it.

Pentaerythritol does not occur in nature but is manufactured by the alkaline condensation of formaldehyde and acetaldehyde. The reaction occurs more or less stepwise with the preliminary aldol condensation to form pentaerythrose followed by a Cannizarro-type reduction to the alcohol:



$$\mathrm{4CH_2O + CH_3CHO} \longrightarrow \begin{array}{c} \mathrm{CH_2OH} \\ | \\ \mathrm{HOH_2C{-}C{-}CHO} \\ | \\ \mathrm{CH_2OH} \end{array} + \mathrm{CH_2O} \longrightarrow$$

$$\begin{array}{c} \mathrm{CH_2OH} \\ | \\ \mathrm{HOH_2C{-}C{-}CH_2OH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

Pure pentaerythritol melts at 261-264° C. (corrected), and occurs as a white crystalline solid resembling granulated sugar in appearance and taste. A technical grade which is about 85% to 90% pure is supplied to the paint and varnish trade, and this has a combining weight of approximately 35.7 instead of the theoretical 34.0.

Unsaturated fatty acid esters of pentaerythritol were prepared over fourteen years ago and were patented by Krzikalla and Wolf (10). Their French patent describes the preparation of the soy bean oil fatty acid ester and the German patent discloses the preparation of a varnish by esterifying a mixture of rosin and linseed oil acids. Bruson (4) mentioned preparing mixed fatty acid esters and states that they have "special drying properties." Gauerke (8) described a method of preparing a complex drying oil by alcoholizing tung oil (the natural glyceride) with polyhydric alcohols including pentaerythritol and then esterifying with linseed oil fatty acids. In 1936 Arvin (1) was granted a United States patent on the soy and linseed esters. Arvin's and Gauerke's processes recommend the use of litharge as an esterification catalyst, but our work has demonstrated that such practice is undesirable as will presently be shown. Arvin prepared paints, enamel, and varnish from his pentaerythritol drying oils and stated that in comparison with the corresponding glycerol esters the pentaerythritol esters were superior with regard to

1. Drying time
2. Gloss
3. Flexibility
4. Hardness
5. Toughness
6. Durability
7. Yellowing

This paper presents data which have been obtained from preparing drying oil acid esters of the technical grade of pentaerythritol, trademarked "Pentek." This product has an average hydroxyl content of 47.2% instead of the theoretical value of 50% for pure pentaerythritol. The reduced hydroxyl content is at least in part caused by the presence of about 15% dipentaerythritol. In addition to original data, because of the unfamiliarity of most American varnish chemists with the work done by the Russians, Drinberg and Blagonravova, edited translations of portions of a few of their articles are included where the data are pertinent.

Film Properties

The drying of the pentaerythritol ester of linseed acids is catalyzed in approximately the same manner as is linseed oil, both cobalt and manganese being powerful driers. However lead is poorly tolerated and ordinary lead naphthenate precipitates out; furthermore it is not as powerful a drier, *per se*, as calcium which is retained well and indeed lead is apparently an anti-drier. These statements are substantiated by Table I which records the tack free drying times (finger-tip method, films on glass) of boiled pentaerythritol-linseed acids ester containing the designated amounts of metal in the form of naphthenates. It may also be noted that the combination