Drying Oils — Past, Present, Future

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The recorded use of drying oil, as such, dates back many centuries, although such oils probably were used for protective purposes prior to these records. Galen, A.D. 230, was one of the first to specifically mention, Nut, Hempseed and Linseed oils as drying oils. He reported that these oils could be coagulated by the use of litharge, white lead and umber. Actius, A.D. 540, set forth the value of Linseed Oil to the arts, especially painting, because of its drying properties. Lucca, in the eighth century, made the first mention of oils in resin varnishes as protective coatings for pictures, although Dioscorides, of the time of Antony and Cleopatra, reported that vegetable oils which had been beaten to a froth and bleached by sunlight had the power of dissolving resins. The use of drying oils was extended by Theophilus in the eleventh to twelfth centuries to the painting itself, although the mixing of the oil with the pigment was done in a very crude way and no knowledge of purifying or refining the oils nor of the acceleration of the drying by driers was recorded. It was not until the thirteenth and fourteenth centuries that the protective value of drying oils was generally recognized in England, France and Germany. One of the first recorded uses of Linseed Oil in varnishes, comparable to the present method of varnish formulation, is credited to Jacobus de Tholeto in 1440. The formula for his varnish was as follows:

> "To make a liquid varnish, take the gum of Juniper (Sandarac) two parts and one part of Linseed oil. Boil them together over a slow fire and if the varnish appears too stiff, add more of the oil and take care not to let it take fire because you would not be able to extinguish it and even if you could extinguish it, the varnish would be dark and unsightly. Let it boil one-half hour and it will be done."

In this formula it is interesting to note that no mention is made of thinning the final product, and it was not until 1750 that the use of thinners, turpentine being the first, was disclosed by Alberti of Madgeburg. In the fifteenth and sixteenth centuries a fuller knowledge of the behavior of drying oils and of the use of driers was gained. This is the period of the old masters of decorative painting and the use of Walnut, Linseed and Hempseed oils is amply recorded. From this time until the beginning of the last century there appear to have been no great advances in the use of these oils. Chinese Tung Oil was first mentioned by the Jesuit, D'Incarville, about the year 1735 as a common adulterant of Chinese lacquer (9).

In 1856, one Christopher Binks read a paper before the London Society of Arts in which he pointed out that no scientific approach had been made to the phenomenon of drying of linseed oil. He proposed to change all this and by systematic work to solve the mystery. In his opinion the theory of drying of boiled oil was erroneous. At that time, according to his statement, it was thought that by boiling oil with a metallic oxide the metal gave up the oxygen and passed it on to the oil, thus causing a pre-oxidation and hastening the ultimate result. This seemed fallacious, Binks said. He began his work by mulling with linseed oil every conceivable substance, painting out glass panels and observing the drying results. How like typical present-day methods this was! Mr. Binks' preliminary report showed that a few metals showed marked activity, others no effect at all. Beyond this he did not go. Of later results we have no record. Perhaps he, too, became bogged in the mire of conflicting results so familiar to all who work with drying oils. I would guess that he gave up this problem to work on something which gave clean-cut results.

Real scientific work on drying oils was begun at the turn of the century and much has been learned. However, the sum total is still small and intensive experimentation must be carried on in the near future in order that drying oils maintain their present position of importance. Improvements must be made and new uses found.

At the present time, linseed is by far the most used drying oil. In 1942, 77% of all oils used in protective coatings was linseed oil. Ninety-three and five-tenths per cent of oils used in making linoleum was linseed and in the printing ink industry linseed accounted for 88.4% of all oils used. In former years the percentage would have been somewhat lower because of greater use of perilla and tung oils. However, the total consumption of drying oils was greater in 1942 than in any other year and the use of linseed far above that of any previous year.

The best way to review the Present of drying oils is to list their uses which contribute to the war effort. Because of the acute shortage of all but linseed and soybean oils, these two materials have been called upon to substitute for many purposes hitherto thought improbable.

The greatest use is, of course, in protective coatings. In this field varnishes are of paramount importance. The shortage of tung oil has led to marked advancement in the use of linseed and soybean oils as replacements for this unique material. Among the first in importance has been the progress in the use of alkyd resins. Resins of this type, based on linseed and soybean oils, have been developed which will perform as satisfactorily as tung oil varnishes in all but some marine uses. In some cases, such as flat olive drab vehicle, the alkyds are far better than tung oil.

Shortly after the beginning of the war maleic anhydride treated linseed and soybean oils appeared on the market and were readily accepted by the varnish trade. This treatment depends on addition of maleic anhydride at an isolated double bond of an unsaturated fat acid. A hydrogen shift takes place from the maleic anhydride to the fat acid and one double bond is used up. This differs from the Diels-Alder reaction of maleic anhydride in which the anhydride adds to a conjugated system and forms a closed ring. In this reaction two of three double linkages are used up and no hydrogen shift takes place.

The maleic treatment imparts to non-conjugated oils the cooking speed of the conjugated type and gives faster dry and greater hardness to varnishes in

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which it is used. In many cases tung oil has been replaced most satisfactorily by this process.

A fairly economical method of alkali isomerization has been developed and conjugated linseed and soybean acids produced in moderate quantities. The glycerol esters of these acids have proved valuable as wood oil replacements. They polymerize very rapidly and have fair drying properties. One drawback to this process, of course, is the necessity of splitting the oil, and carrying on the reaction with the soap formed. A good method of conjugation without splitting has long been desired. Progress in this direction has been reported at the recent A. C. S. meeting in Pittsburg. The experiments reported utilized certain silicates as catalysts and conjugation to the extent of about 25% was indicated.

Solvent extraction of oils has provided the so-called segregated oils. This extraction may be carried out on either bodied or limpid oils. The process utilized most widely today makes use of bodied linseed or fish oils. The bodied oil is treated with a solvent and the polymerized (insoluble) portion is separated from the unpolymerized (soluble) portion. The insoluble of course includes the most unsaturated, fast-drying glycerides. These segregated oils have been most valuable in the production of hard fast-drying varnishes. They are especially adapted for use with dehydrated castor oil since they are brittle and need plasticizing. The castor oil, on the other hand, tends to retain a tack on drying and this is overcome by the segregated oil.

For years varnish makers have sought a method for shortening the bodying time of linseed oil. Drier metals were used but dark, cloudy oils resulted. Diphenyl showed fair catalytic activity but a practically black oil resulted. Sulfur compounds, both organic and inorganic, were also open to the same criticism. In the past few years, however, several linseed oil polymerization catalysts have been introduced which do not darken the oil. In fact, these catalysts cut the bodying time 30 to 50% and give a lighter colored oil, of lower acid value. The kettle loss is also reduced. These catalysts have helped the varnish processor save time and raw material when both are needed.

The role of dehydrated castor oil in replacing tung oil is too well known to all of you to need repeating here. Needless to say, it has been invaluable and will undoubtedly be a basic raw material for protective coatings for a long time to come.

The war has brought on a great demand for water-thinned paints both for military and civilian use. A great deal of work has been done to develop suitable vehicles; one such was a water soluble drying oil which is being widely used. Other vehicles consist of emulsified oils, varnishes and resins. Water paints are now approaching the quality of oil flats and should enjoy a large sale in the future. Much improvement should be made, however.

Linseed and soybean oil partial esters and esters of lower alcohols are being used as plasticizers for cellulose lacquers, resin solutions, and plastics. Specially treated drying oils are also being used as castor oil substitutes for the above purposes as well as for hydraulic system fluids.

Partial esters of alcohol having four or more hydroxyl groups have proved very interesting as plasticizers but the alcohols have been restricted to such an extent that only moderate amounts of such materials have been sold. The same holds true of these completely esterified polyhydric alcohols as varnish oils.

Turning from protective coatings we find that the drying oils are bearing to a small extent the load of rubber replacement. Factice has been used in greater amounts than ever to extend rubber in products where high strength is not required. Several specially treated, vulcanized oils have appeared on the market and are said to be efficient in extending rubber up to 10% even in tire casings without appreciable loss in quality.

Elastomers of the Norepol type have been found to be suitable as rubber substitutes for many purposes, especially for gaskets and sealing compounds. Lack of production facilities and shortage of oils has prevented wider use of such materials. Another recently announced material similar in nature is Norelac. This resin-like polyamide is made by the same basic process and looks most interesting as a coating, laminant, or heat sealing plastic.

Fairly suitable sealants for puncture-proof gasoline tanks have been developed from drying oils but because of the rapid expansion of the synthetic rubber industry are little used.

The separation of saturated from unsaturated fatty acids by distillation has been commercially successful and it is now possible to obtain triglycerides of such acids. By varying the source of the acids and the proportions of acids in the ester, it is possible to supply more or less tailor-made oils.

Fatty acid amines, amides and nitriles are finding a wide variety of uses and are proving a valuable basic raw material for many processes. Some present uses are as plasticizers, insect repellents, flotation agents and chemical intermediates.

It's hard to predict the future except in the light of past experience or present need. Future needs are controlled by unforeseen circumstances and therefore are difficult to predict. With this qualification I should like to state a few developments which I think should or may take place in the drying oil field in the future.

1. The breeding of new plant varieties to give higher I. V. or higher concentration of certain fatty acids. Recent work at the North Dakota Agricultural College shows that the linolenic acid content of linseed oil is higher than previously believed. Examination of data collected indicates that there may be a possibility of breeding a flax variety that would give much higher linolenic acid and lower linoleic acid content. The work is going forward. A similar development on soybeans would give a rich source of linoleic acid.

2. The commercial development of new varieties of hitherto unavailable oil seeds. Two worth mentioning are Chia seed and Garcia nutans. Both seeds contain oils having valuable properties and it should be possible to develop the growing of these seeds in the same manner as has been the case with oiticica.

3. Greater use of segregated oils in protective coatings and as raw materials for further chemical processing.

4. Further development of specially constructed triglycerides by separation of fatty acids and reforming.

5. New synthetic binding materials which utilize drying oil acids as basic building blocks. Recent work on maleinized oils and on dimer and trimer acids have

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