

I. Then $f = 100 - (b + c + d + e)$
Let $g = \%PO_4$ in total mono and di dodecyl phosphate

$$\text{II. Then } g = \frac{a \times 100}{f}$$

Let $X = \% \text{ di dodecyl phosphate}$

$$\text{III. Then } X = \frac{35.67 - g}{35.67 - 21.85} \times 100$$

Let $Y = \% \text{ mono dodecyl phosphate}$

IV. Then $Y = 100 - X$

However X and Y are both based on the total amounts of mono and di esters but since there are only $f\%$ of such compounds, X and Y must be multiplied by $.01 f$ to give percentages based on the original sample.

Example :

By determination $a = 17.04\%$ (combined PO_4)
 $b = .90\%$ (ash)
 $c = 0.00\%$ (water)
 $d = 25.5\%$ (free dodecyl alcohol)
 $e = 1.51\%$ (free H_3PO_4)

$$\text{I. } 100 - (b + c + d + e) = f$$

Substituting $f = 100 - (0.90 + 0.00 + 25.50 + 1.51)$
 $f = 72.09$

$$\text{II. } \frac{a \times 100}{f} = g$$

$$g = \frac{17.04 \times 100}{72.09}$$

$$g = 23.64$$

$$\text{III. } X = \frac{35.67 - g}{35.67 - 21.85} \times 100$$

$$X = 87.05 \text{ (\% di dodecyl phosphate based on phosphate esters alone)}$$

$$\text{IV. } Y = 100 - X$$

$$Y = 100 - 87.05$$

$$Y = 12.95 \text{ (\% mono dodecyl phosphate based on phosphate esters alone)}$$

$$87.05 \times .01 \times 72.09 = 62.75 \text{ di dodecyl phosphate based on original sample}$$

$$12.95 \times .01 \times 72.09 = 9.34 \text{ mono dodecyl phosphate based on original sample}$$

Analysis :

1.51% free H_3PO_4
25.50% free dodecyl alcohol
0.00% water
.90% ash
62.75% di dodecyl phosphate
9.34% mono dodecyl phosphate

Total 100.00%

The same method applies for other fatty phosphates providing the proper factors are applied in equation III.

Summary

A method is presented for the determination of mono and di alkyl phosphates in the presence of the contaminants usually present when the sample is prepared by the reaction of P_2O_5 or H_3PO_4 on fatty alcohol. Total PO_4 , free H_3PO_4 , hydroxyl, ash, and water are determined by simple methods and the percentage of mono and di esters are calculated therefrom.

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Polymer Formation From Natural and Synthetic Drying Oils

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General

THE natural triglyceryl esters of importance in polymer chemistry are predominantly the esters of the octadecadienoic and octadectrienoic isomers characteristic of linseed and tung oils, respectively. The polymerized vegetable oils sold commercially for use in various phases of the protective and decorative coatings industries (paints, varnishes, lacquers, printing inks, linoleum, binding agents, etc.) are not high polymers. The maximum polymeric form found in such oils has been the tetramer, and the average form would be approximately that of the dimer; however, the final utility of these oils in coatings depends in some measure on their ability to form high polymers.

When such drying oils are spread out in thin films and allowed to "dry" or otherwise processed to form

gels the products are in a large degree insoluble and infusible and relatively chemically resistant. Their examination is subject to the same limitations as is that of the polyesters, which are now clearly recognized as high polymers. It should be noted, however, that the resultant poly-films or gels contain varying amounts of smaller molecular species interspersed therein. It is probably this characteristic which has resulted in the colloidal approach to the problem by some workers in the field. The view now generally held is that the colloidal phenomena are a secondary problem, and result from the formation of a polymeric phase (1).

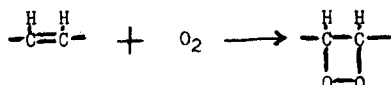
The vegetable oils are a relatively cheap source of raw material, so that their total yearly product value possibly does not approach that of the synthetic

plastics. The quantity used, however, is tremendous—roughly seven hundred million pounds per year in the protective coatings and similar industries.

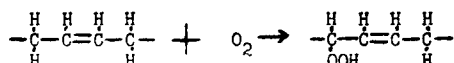
Mechanism of Polymerization

The ability of an oil to polymerize or to dry in films is related to its unsaturation, since it is the double bonds which are the reactive centers about which polymerization takes place. Many mechanisms have been advanced, and due to the complex nature of the drying oils many different reactions are indeed involved.

Polymerization in the Presence of Oxygen: The "drying" of films or the preparation of "Blown" or "Oxidized" vegetable oils are representative of such polymerization. In either case the initial step has been classically held to be the formation of peroxides:



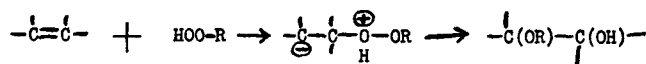
Recently, however, E. H. Farmer and co-workers (2) have shown that the initial product at ordinary temperatures is more likely a hydroperoxide in which oxygen has been added at the methylenic carbon atom in the alpha position to a double bond:



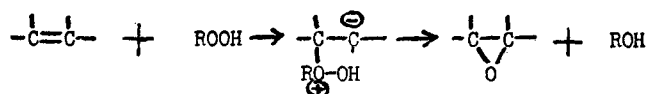
Speaking of the formation of peroxides at the double bond, Farmer wrote: "This view cannot be maintained; the disappearance of olefinic unsaturation rarely keeps pace with the incorporation of oxygen, although under usual conditions of reaction severe diminution of unsaturation due to secondary reactions often occurs."

Although hydroperoxides decompose readily some (including the methyl oleate product) are sufficiently stable to be isolated; in the case of polyolefins, however, decomposition apparently takes place side by side with their formation, rendering the mechanism difficult to prove directly. Farmer's view is that autoxidation occurs through the hydroperoxide mechanism regardless of temperature, type of catalysis, etc. Several basic secondary reactions are presented to explain the presence of observed products of the oxidation of olefins; among them are:

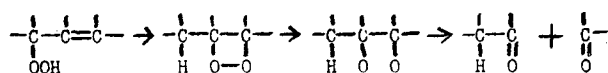
(a) Polymerization to give ether-type dimerides—



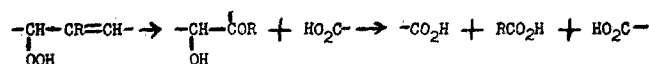
(b) Reaction of hydroperoxide with a double bond—



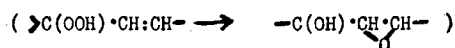
(c) Scission of carbon chain at the double bond—



(d) Subsidiary scission between ethylenic bond and α -C atom—



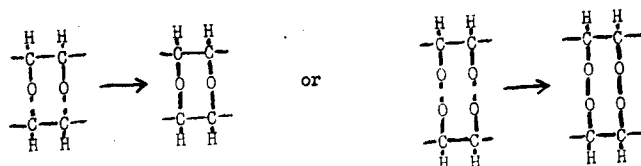
Morrell and his co-workers (3) attacked the validity of Farmer's work, particularly as applied to drying oils, declaring that according to Farmer's mechanism one-half of the total oxygen absorbed by methyl linoleate would be present as -OH whereas their analyses indicated only one-quarter present as such. They apparently considered, however, only one



of the possible secondary reactions described by Farmer. Further, there was disagreement as to the reliability of the analytical methods used to identify the products obtained, but this disagreement was not rigidly resolved.

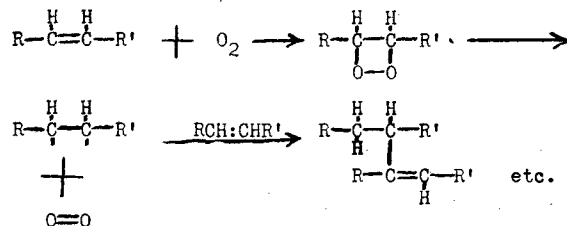
Atherton and Hilditch (4) studied the union of oxygen with methyl oleate at 20° and 120° C. The products were separated by absorption on silica gel and portions of the separated products further oxidized with KMnO_4 and the quantity and nature of the mono- and di-carboxylic scission products determined. From the union at 20° a substantial portion of suberic and octoic acids was found in the scission products, indicating that peroxidation had to a large extent occurred at the $-\text{CH}_2-$ group adjacent to a double bond. From the oxidation of the products of the 120° reaction only traces of suberic and octoic acids were found; nonoic and azelaic acids were present in quantity, and also products indicating changes of a more complex nature. This indicates that direct peroxidation of the double bond predominates at higher temperatures, but does not obviate the possibility that the initial step consists of hydroperoxidation which is immediately followed by decomposition.

Whatever the nature of the initial step, polymerization could subsequently take place in such a manner as to result in either oxygen-linked or addition polymers. It was suggested by Marcusson (5) and by others that peroxides or similar oxidation products could form oxygen-linked polymers:



That such structures are important in blown oils or dried films has never been confirmed. The products of a hydroperoxide reaction with a double bond (see a and b above) would be in better agreement with the observed formation of epoxy and hydroxy groups as well as polymers when vegetable oils are oxidized with air.

It is Power's view that the role of oxygen is primarily one of activation so far as such polymerization is concerned and that after activation the polymer formation proceeds through the conventional vinyl mechanism, or at least that such a mechanism plays a role more important than heretofore recognized (6).



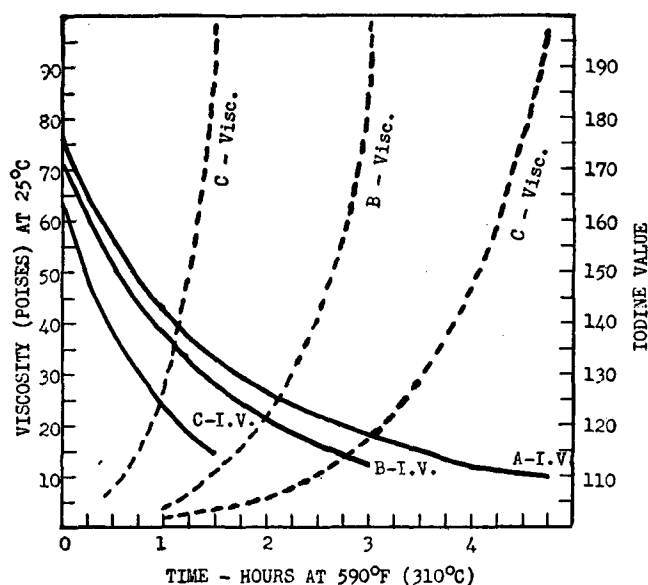


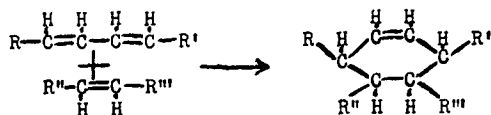
TABLE SHOWING IODINE VALUE-VISCOSITY RELATIONSHIP FOR THE POLYMERIZATION OF:

A—Alkali Refined Linseed Oil; B—Commercial Fast-Bodying Linseed Oil "B"; C—Commercial Fast-Bodying Linseed Oil "C".

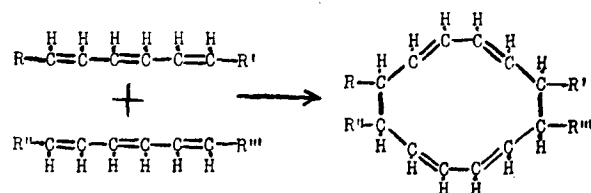
Heat Polymerization of Drying Oils: The "bodying" of drying oils for the preparation of varnishes and similar materials is representative of such polymerization. The polymerization takes place readily in vacuo or inert gas at temperatures in the vicinity of 300° C.; somewhat lower temperatures are employed in the case of tung oil. Due to the relatively high temperatures for the heat bodying of drying oils considerable quantities of decomposition products are obtained.

It is still general practice in the varnish industry to carry out the polymerization in open kettles, and here oxygen plays a role of activation since it is a matter of common observation that drying oils will polymerize at a given temperature more rapidly in the open than under vacuum or inert gas. However, the nature of the polymers obtained from open or vacuum-inert gas systems is essentially similar, although the wetting and other properties are greatly affected by the varying amounts of decomposition products present. The exclusion of oxygen simply prevents the formation of oxidation products and the use of vacuum or inert gas flow removes other volatile decomposition products. In either case the possible oxygen-linked structures discussed in the preceding section are of no importance.

Considering the step of activation to have been accomplished, most schemes postulate the formation of cyclic dimers (7). Dimerization might take place between fatty acid chains through a Diels-Alder reaction:



Or for a triply unsaturated glyceride, such as tung oil, there would be the possibility of the formation of the cyclic structure:



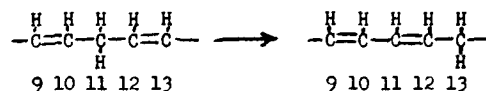
The formation of trimers and tetramers is similarly postulated.

Note that such schemes are valid only for conjugated systems, whereas most drying oils (except tung oil) contain relatively small quantities of the conjugated isomers. Fortunately, at the temperatures necessary for polymerization a shift of the double bonds in the fatty acid chains occurs in such a manner as to result in the conjugated form. The percentage of conjugated isomers builds up to a certain point before appreciable polymerization takes place. This preliminary shift to a conjugated structure has been investigated by absorption spectroscopy and other methods (8).

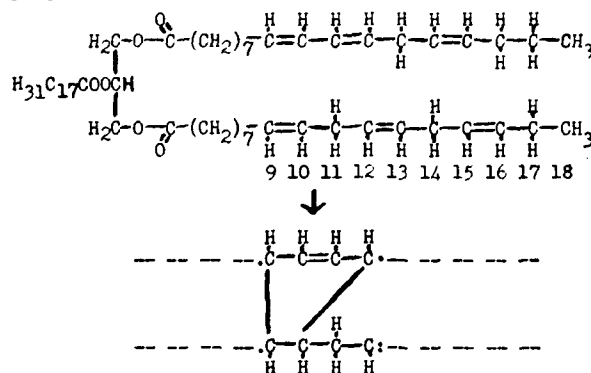
As an indication of this shift reference can be made to a simple data table (Experimental Column A) and the accompanying graph showing the viscosity and iodine value for a sample of linseed oil polymerized at 590° F. It will be noted that the iodine value has dropped 60 units at the end of two hours, while the viscosity has only increased to 6 poises, and that the major portion of the viscosity increase (indicating polymerization) takes place subsequently with comparatively little corresponding decrease in iodine value. Since it can be demonstrated that in a conjugated fatty acid one of the double bonds is relatively insensitive to the addition of iodine, the large decrease in iodine value without corresponding polymerization can be attributed to conjugation.

Adams and Powers (9) suggested the following sequence of events for the heat polymerization of drying oils:

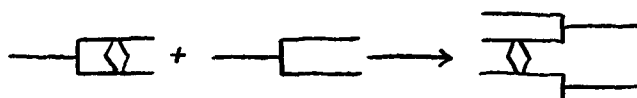
(a) Rearrangement to conjugated diene structure—



(b) Formation of cyclic structures between chains, primarily between chains of the same glyceride ("intrapolymers")—



(c) Ester interchange between an intrapolymer and another glyceride molecule to result in polymers—



Time— Hours at 590°F.	Viscosity (Poises)	I. V.	Viscosity (Poises)	I. V.	Viscosity (Poises)	I. V.
0	0.5	174.6	0.6	173.4	0.8	167.2
1/2	1.0	157.5	1.6	152.2	5.2	133.8
1	2.0	142.0	4.3	135.2	28.0	118.9
1 1/2	4.0	130.8	9.0	126.5	98.5	113.8
2	6.0	126.6	22.0	121.1
3	18.0	120.3	98.5	112.3
4	50.0	113.9
4 1/2	98.5	108.7

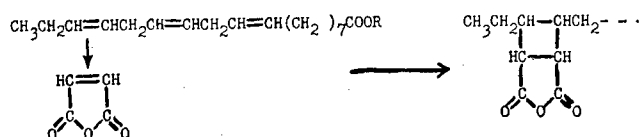
TABLE SHOWING IODINE VALUE-VISCOSITY RELATIONSHIP FOR THE POLYMERIZATION OF:

A—Alkali Refined Linseed Oil; B—Commercial Fast-Bodying Linseed Oil "B"; C—Commercial Fast-Bodying Linseed Oil "C".

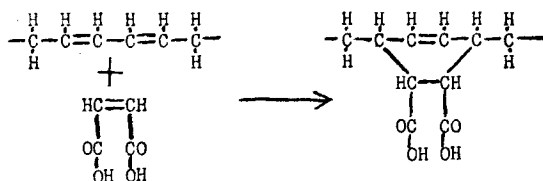
The functionality concept (10) may also be applied to the polymerization of drying oils. No fatty acid, as such, has been demonstrated to form more than a dimer. In other words, they are apparently monofunctional and are incapable of further reaction after their association to form a dimer. For bifunctional compounds, the dimer will retain the same functionality as the monomer. However, in the case of tri- or more functional compounds the functionality actually increases with increasing Degree of Polymerization; this situation is encountered in certain of the "polyester" resins. 3-Functional compounds become 4- at the dimer stage, 5- at the trimer stage, etc. Thus, fatty acids or their methyl esters will be expected to form only dimers. Di-esters of the fatty acids will polymerize to a limited degree if the acids are of sufficiently unsaturated character, while the triglyceryl esters are capable of polymerization as previously indicated. Further, the functionality increases when fatty acids are esterified with higher polyhydric alcohols such as pentaerythritol, sorbitol, polyallyl alcohol, etc., and polymers of improved properties are obtained, which is the basis for a class of "synthetic" drying oils. This is not, however, to state that the functionality increases linearly for each OH of a polyhydric alcohol or for each additional double bond in the fatty acid chain. The increase in functionality and prediction of the gel stage for polyesters and similar compounds has been treated mathematically by Flory (11).

Chemically Processed Oils for Industrial Use ("Synthetic" Drying Oils)

Dibasic Acid Condensation Products: These are the unsaturated dibasic acid (or anhydride) adducts of unsaturated drying or non-drying oils. One type is claimed to be the reaction product of unsaturated dibasic acids with isolated double bonds of fatty acids or their esters (12):

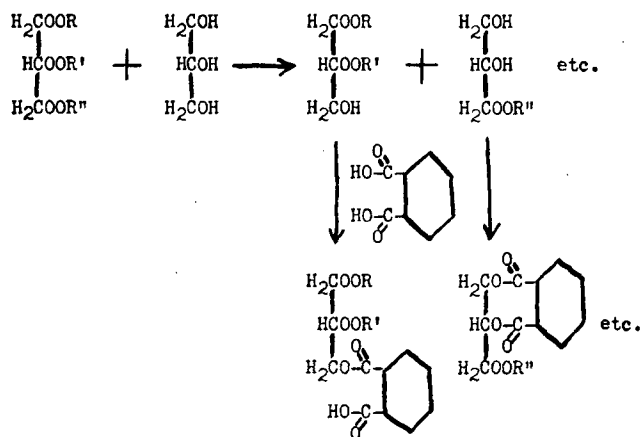


Another type claims the products of a diene synthesis, which chemically must be considered as taking place upon a conjugated system (13):



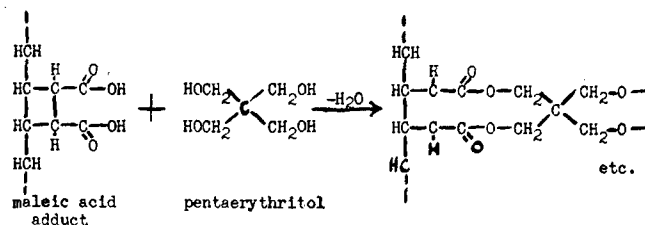
These adducts polymerize readily, particularly in the presence of oxygen. The polymers are water dispersible in alkaline emulsions (polar groups) and find application in the modern water-thinned water paints and elsewhere.

Alkyd Type Condensation Products: Vegetable oils (drying or non-drying, but necessarily unsaturated) are reacted with a polyhydric alcohol to form mono- or di-glycerides, and the free hydroxyls are then reacted with a dibasic acid or anhydride thereof to form mixed esters (14):

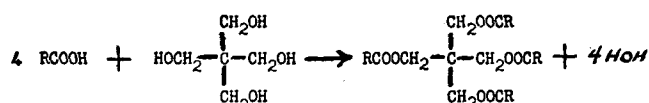


It can readily be seen how further reaction can take place with unreacted hydroxyl groups and also at the double bonds to result in three-dimensional polyesters of high M.W.

A modification of this type, which should result chemically in quite different products, is the esterification of the free acid groups of the dibasic acid adducts previously discussed with a polyhydric alcohol. It is difficult in practice to avoid the formation of insoluble dibasic acid-polyhydric alcohol resins by this procedure; further, in many cases the final product of such a reaction is all but indistinguishable from the true alkyd type, presumably through a mechanism of ester interchange. There is, however, a considerable quantity of patent literature (15). Polyester formation in this case could be pictured:

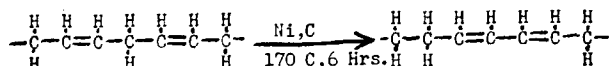


Fatty Acid Esters of Polyhydric Alcohols: As previously mentioned, the higher polyhydric alcohol esters are useful as polymerizing oils. Such "synthetic" (as opposed to natural) glycerides are prepared by the direct reaction of fatty acids and pentaerythritol (2-bishydroxymethyl-1,3 propanediol), poly-pentaerythritols ($-\text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\text{C}-$, etc.), sorbitol (1,2,3,4,5,6 hexanehexol) and many others (16).



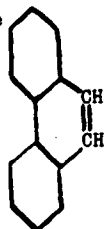
Catalytically Isomerized Oils: Biochemical investigations first indicated that the acids resulting from the alkaline saponification of natural oils were conjugated to a degree slightly higher than their state in the natural oil. This led to patents in which alkaline catalysts were used to isomerize fatty acids, which were subsequently re-esterified; the process (17) is somewhat indirect and cumbersome for commercial application, but has reportedly been worked.

Other patents which claim the direct conjugation of oils by various catalysts, such as Al_2O_3 , have appeared from time to time, but the catalysts claimed frequently have little more effect than heat alone, except as to decomposition of the oil. More recently the Northern Regional Research Laboratory at Peoria has developed a Nickel-Carbon catalyst and process (18):

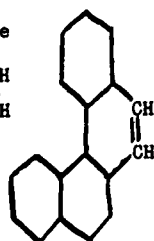


Catalytic Fast-Bodying Oils: The simplest in treatment of the chemically processed triglycerides are those to which a minor amount of a polymerization catalyst has been added, which causes them to body much more rapidly than the uncatalyzed oils. One process (19) claims as such a catalyst the "oxidation products of coal-tar hydrocarbons having the formula $\begin{array}{c} \text{R}-\text{CH} \\ | \\ \text{R}'-\text{CH} \end{array}$ where R and R' are aromatic nuclei, in amounts of .05% to 0.5%. Hydrocarbons having this general formula would be:

Phenanthrene



Chrysene



etc.

The oxidation products themselves are not named, but inferentially would be the corresponding quinones. Oxidative derivatives of anthracene seem to be specific catalysts. One patent claims β -methyl anthraquinone and like compounds (20). Another claims specifically diphenol carboxyl anthracene (21).

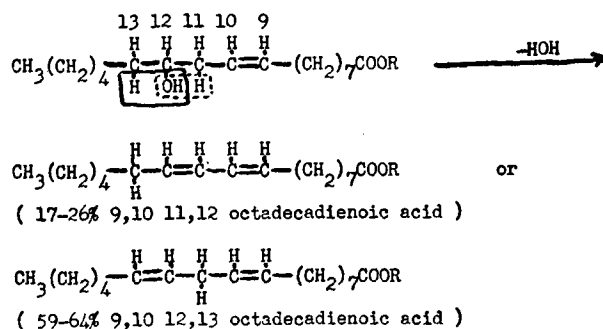
It is interesting to note that such substances belong to a class generally regarded as polymerization inhibitors. It can easily be demonstrated that both β -methyl anthraquinone and diphenol carboxyl anthracene are as efficient in the inhibition of the polymerization of styrene as is hydroquinone, a recognized stabilizing agent (see *Experimental*).

No rigid explanation of the catalytic activity of the anthraquinones and similar compounds on the polymerization of drying oils has ever been given. In view of the dehydrogenation of hydrocarbons by certain aromatic quinones, however, it seems reasonable to propose that they act to catalytically isomerize the double bonds of the fatty acid chains to the conjugated positions. As support for this view the data given in the table under *Experimental* can be cited. It can be seen that the polymerization proceeds for two commercial catalytic oils (Columns B and C; see also graph) in essentially the same manner as for the

uncatalyzed linseed oil (Column A) as regards iodine value-viscosity relationship; however, the same low iodine value stage (approximately 130) preceding appreciable polymerization is reached much more quickly. This would be in accord with the catalytic isomerization view; spectroscopic data proving conjugation during the early stages of the heating in excess of that encountered for an uncatalyzed oil would be sufficient to confirm this.

Dehydrated Castor Oil: Castor oil, a non-drying oil, has long been valued for its lubricating and hydraulic properties. It is not miscible with petroleum oils, a serious disadvantage since where mixing occurs the lubricating properties of the film break down. Many years ago it was discovered and recognized that the dehydration of castor oil rendered it soluble in mineral oils, and it was further recognized that such dehydration could lead to drying oils (22). The fact that the classical dehydrating catalysts could be used in the process was also disclosed in the literature of the same period (23). During the first World War considerable quantities of mineral-soluble castor oil were used in the lubrication of aircraft engines, etc. ("Castorlubrin"). The early commercial methods employed for the dehydration resulted in only partial dehydration and the resultant oils were still non-drying in the usual sense. Thus, it was only comparatively recently, and under the pressure of an unstable chinawood oil market, that it became generally recognized that excellent drying oils of good polymerization characteristics could be obtained from castor oil. Improved processes were patented about 1930 (24). There are probably more patents regarding the dehydration of castor oil than there are in all other phases of drying oil chemistry; comparatively few are of basic nature. The processes and product have been vastly improved, however; several patents may be cited to typify the development of the technique (25).

Chemically, the dehydration comprises the removal of OH and an adjacent H from the ricinoleic (12-hydroxy 9,10 octadecenoic acid) portion of the triglyceride. Fortunately, castor oil is one of the relatively few naturally occurring triglycerides which is composed largely of one acid, the acid portion being largely ricinoleic. The dehydration may proceed in two ways, according to whether the 11 or 13 hydrogen is removed; it was formerly believed that the greater part of the resulting dienoic acid was conjugated, but according to Priest and von Mikusch (26), the non-conjugated isomer predominates:



One patent (27) teaches the dehydration of castor oil by using as a catalyst an alkyl sulfate, specifically 0.2-0.5% diethyl sulfate, and heating under vacuum at temperatures above 500°F .

Other treatments of vegetable oils to give polymerizable materials should be mentioned. Hydroxylation, usually by blowing with air, followed by dehydroxylation in the presence of dehydrating agents is employed on linseed and soybean oils (28). Physical processes, such as solvent segregation, are also employed. One type (29) depends on the well known solubility difference of similar molecular species having different molecular weights. In this process the oil is first partially heat-bodied, then extracted with acetone or similar solvents to remove the unpolymerized portion. Since this portion contains the more saturated and less reactive components, the remainder is a harder-drying and faster-polymerizing material.

A more recent development is the liquefied hydrocarbon (propane, etc.) method wherein the solvency is apparently specific for a given degree of unsaturation; this makes possible the segregation of fatty oils into unsaponifiable, low iodine value, and higher iodine value fractions without affecting the chemical constitution of any of the parts.

Experimental

Viscosity-Iodine Value Relationship for the Polymerization of Linseed Oil With and Without Catalysts: 3,500 gm. of alkali refined linseed oil was polymerized at 590° F. (310° C.) to a Gardner-Holdt viscosity of Z-5 (98.5 poises) in a 1½-gallon stainless steel kettle. Samples were withdrawn at intervals and the viscosity and iodine value determined. Data is recorded in the accompanying table, Column A. 3,500 gm. of commercial fast-bodying oil "B" (Column B) and 3,500 gm. of commercial fast-bodying oil "C" (Column C) were polymerized and examined in the same manner.

Inhibition of the Polymerization of Styrene by Drying-Oil Polymerization Catalysts: 20-ml. samples of styrene monomer (from which the inhibitor had been removed by careful washing with 10% aqueous KOH and water) were placed in glass ampoules. To one was added 0.1% hydroquinone, to the second

0.1% β -methyl anthraquinone, and to the third 0.1% diphenol carboxyl anthracene; to a fourth (Control) no inhibitor was added. All four tubes were immediately sealed off and placed in a 60° C. bath for 2 hours. They were permitted to stand in the sunlight at room temperature for four weeks.

At the end of this period the control was very viscous, so that several minutes were required to note any flow when the ampoule was held at 90° to the vertical. The three tubes containing additives were apparently little polymerized, all three being very limpid.

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The Digestibility of Fats — A Correlation of Experimental Data*

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THE digestibility of fats has been studied extensively in a number of laboratories over the past 30 years, the major portion of the data having been collected by several groups of workers, each of which used some one type of experimental subject. In one set of experiments digestibilities were compared in two types of subjects (1, 2). Dogs were employed in several laboratories in some of the very early work (3, 4). The first intensive studies were conducted in the laboratories of the Office of Home Economics of the U. S. Department of Agriculture, by Langworthy, Holmes and Deuel, who reported the

digestibilities in adult humans of a wide variety of natural and hydrogenated fats in a series of publications over a period of more than ten years (5-16). Their work, a large portion of which was done during the fat shortage following the first World War, included practically every fat which could be considered a potential source of food. More recently there has been a series of publications by Hoagland and Snider of the Animal Nutrition Division, Bureau of Animal Industry of the U.S.D.A., reporting the digestibilities of some of the more common animal and vegetable fats, shortenings, and several synthetic saturated triglycerides in albino rats (17-21). One of the most significant investigations to date was con-

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