

# Dehydration of Castor Oil

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DEHYDRATED castor oil is the best known and most widely used of all the oils commonly termed improved, treated, or "synthetic" drying oils. It has, in fact, come to be regarded almost as a natural drying oil. The dehydration of castor oil represents the conversion of an absolutely non-drying oil to an oil of highly desirable drying properties, a dramatic fact in itself. This conversion is made possible by the unique chemical composition of raw castor oil, as will be later discussed. The commercial utilization of dehydrated castor oil in the United States dates from about 1938 and resulted largely from the uncertain supply and high price of tung oil. Table I shows the percentage of total castor oil consumption as dehydrated castor oil consumed. The rapid growth and relatively stable consumption in recent years are obvious.



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The historical background of dehydrated castor oil is of considerable interest. Patents dating from about 1900 indicate that it was realized even then that drying properties could be developed in castor oil under the influence of heat (1). However castor oil was valued as a lubricant, and the development of the gasoline engine caused most of the work then done to be directed toward making a mineral-oil-soluble castor oil; raw castor oil is not to any appreciable extent miscible with petroleum oils, and lubricating properties may be adversely affected where mixing occurs. Partial dehydration may be employed to impart this miscibility so most of the processes employed were

essentially of this nature and hence related to the dehydration of castor oil as it is known today.

By about 1915 the chemistry of the dehydration of castor oil seems to have been reasonably well understood. The fact that heating castor oil in the presence of catalysts (including phosphoric and sulfuric acids) split out water and resulted in products of increased unsaturation was recognized by Rassow (2). Fokin reacted ricinoleic acid with  $P_2O_5$ ; he identified the products as conjugated and non-conjugated isomers of linoleic acid and compared the product with the acids from linseed and tung oil (3).

So far as the development of a substitute drying oil is concerned however, this work apparently went unheeded until the late 1920's, when the lack of tung oil had already become an acute problem in Germany. Scheiber claimed a product having about 90% conjugated acids; the process consisted essentially of dehydration of ricinoleic acid and subsequent re-esterification (4). Practically speaking, such a process would obviously be an unattractive proposition commercially; consequently attention was redirected to the older soluble-oil processes where the oil itself was heated with catalysts. Such direct processes were soon applied to the production of drying oils (5). Over the years literally hundreds of patents have been granted dealing with various phases of the dehydration of castor oil, as even a cursory search discloses.

As previously mentioned, the unique chemical composition of castor oil is basic to the chemistry of dehydrated castor oil. Nearly 90% of the fatty acids of castor oil are hydroxy acids, in the main comprised by ricinoleic acid and a minor percentage of dihydroxystearic acid (see Table II). When castor oil is heated in the presence of certain catalysts, the elements of water are split from the ricinoleic acid chain. This removal of the hydroxyl group and an adjacent hydrogen atom results in the formation of a new double bond in the fatty acid chain. By comparing the structure of ricinoleic acid and the two isomers of linoleic acid the possibility of synthesizing the latter is obvious.

TABLE I

Consumption of Castor Oil and Dehydrated Castor Oil  
(Quantities in thousands of pounds)

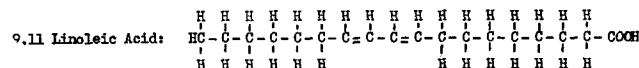
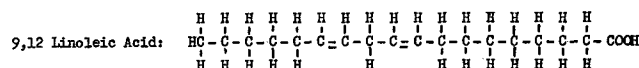
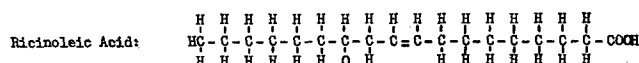
Year	Total Castor Oil Consumed	Dehydrated Castor Oil Consumed	Percentage Consumed as Dehydrated
			%
1949.....	94,472*	31,435*	33.27*
1948.....	108,345	41,102	37.94
1947.....	97,271	30,699	31.56
1946.....	80,032	27,225	34.02
1945.....	141,876	49,047	34.57
1944.....	186,463	69,361	37.20
1943.....	69,740	15,609	22.38
1942.....	91,097	46,137**	50.64
1941.....	89,920	44,240**	49.20
1940.....	54,046	24,368**	45.09
1939.....	41,090	11,439**	27.84
1938.....	28,160	5,792**	20.57
12-year totals.....	1,082,512	396,454	36.35 (avg.)

Source: Adapted from *Animal and Vegetable Fats and Oils*, Bureau of the Census 1941, 1945, 1946, and 1950.

\*Totals from quarterly and monthly reports for 1949 (subject to revision).

\*\*System of reporting changed during 1942. Figures prior to 1942 are for castor oil as such used in paint and varnish and assume most of this was used as dehydrated castor; 1942 consumption includes second 6 months reported as dehydrated castor consumed, plus amount reported for first 6 months as castor oil used in paint and varnish.

Carbon No.: 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1

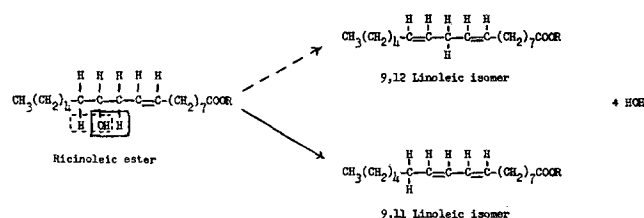


The basic reaction, then, in the dehydration of castor oil can be pictured as in Figure 1. The amount of water evolved correlates reasonably well with the theoretical as calculated by decrease in hydroxyl num-

TABLE II  
Approximate Fatty Acid Composition for Typical Raw and Dehydrated Castor Oil

	Castor Oil	Unbodied Dehydrated Castor Oil
Saturated Acids, %.....	0.5	0.5
Hydroxy Acids, %.....	88.0	5.0
Oleic Acid, %.....	7.5	7.5
9,12-Linoleic Acid, %.....	4.0	65.0
9,11-Linoleic Acid, %.....	....	22.0

ber. After a study of a number of dehydrated castor oils and fatty acids Priest and von Mikusch estimated that the conjugated 9,11-linoleic acid was present only to the extent of 17-26% whereas the normal 9,12-linoleic acid comprised 59-64% (6). These values were calculated in a straightforward manner, using the observed hydroxyl value to calculate the theoretical unsaturation; this was used to calculate the diene value which should result if all the new double bonds

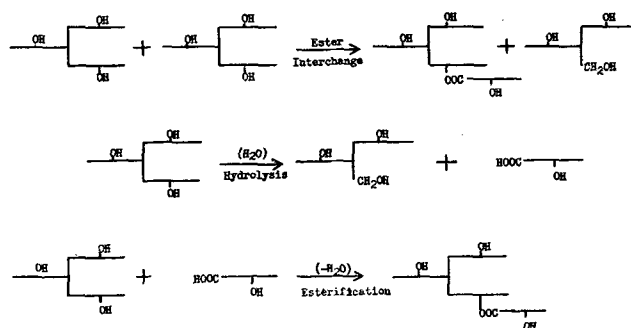


were in the conjugated position and, in turn, compared with the diene value actually obtained. The Hanus number was reported to be a reasonably accurate gauge of total unsaturation. The amount of conjugation present—roughly a maximum of 30%—was in sharp contrast to the 75% reported earlier by Boeseken and Hoevers (7) and the 90% claimed by Scheiber.

It should be noted that in the oils studied by Priest and von Mikusch were included some which appear to be incompletely dehydrated as well as bodied oils in which the percentage of conjugation would be materially reduced during polymerization. Analysis of current commercial unbodied dehydrated castor oils by the same method indicates the percentage of conjugated isomers generally approaches the maximum reported, i.e., about 30%. In connection with incomplete dehydration it is found on dehydrating castor oil that the acetyl value rarely approaches 0 but rather tends to reach a limiting value of say 5-10 even under severe conditions. Several explanations have been offered for this behavior. The residual acetyl value may be due to dihydroxystearic acid, either as originally present in raw castor oil or as formed *in situ* during the dehydration. It seems unlikely that a simple equilibrium resulting in unaffected ricinoleic acid is the explanation since a limiting value is approached where the conditions (particularly high vacuum) are such as to remove any water formed.

Subsidiary and side reactions take place during the dehydration of castor oil, and Kappelmeier (8) believes these may be of sufficient importance that the hydroxyl value should not be taken as a measure of the dehydration. That a difficultly saponifiable substance is formed during the dehydration at atmos-

pheric pressure is evident from the fact that considerably higher saponification values are obtained on prolonged boiling or by using butyl alcoholic KOH, etc.; also the methyl esters saponify more easily and show higher hydroxyl values than do the corresponding dehydrated oils. Vacuum techniques were stated to lessen the disparity noted but not to guarantee complete dehydration. While the exact extent to which the various possible side reactions occur depends on the conditions employed and further is rather difficult to determine in an absolute sense by purely analytical means, it is certain that interpretation of hydroxyl value too literally as a measure of residual ricinoleic hydroxyl is unwarranted.



A direct ester interchange is possible (see Figure 2), of somewhat different character than the ordinary interchange of acid radicals among triglycerides, such as is known to occur; this would result in a mono-glyceride and an ester of the secondary alcohol group on the ricinoleic chain. At any rate, a stepwise process of hydrolysis and esterification could occur and the products would be the same. The secondary alcohol ester is known to be more difficult to saponify than is one from a primary alcohol; the esters thus formed would in effect represent "protected" hydroxyl groups.

The increase in acid number during dehydration probably reflects the hydrolysis as shown; however the situation is further complicated by the fact that acids, etc., can arise by thermal decomposition and splitting during the dehydration. The odor of acrolein is amply evident during the dehydration. In the distillate from the dehydration both 10-undecenoic or undecylenic acid [ $\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{COOH}$ ] and heptanal [ $\text{CH}_3(\text{CH}_2)_5\text{CHO}$ ] have been found, in addition to fatty acids.

The synthesis of a triply conjugated oil from a wholly conjugated dehydrated castor is of course theoretically possible, and indeed it has been claimed to be accomplished (9). However this has not been confirmed; samples purporting to result from the process have been found to contain substances present only in natural tung oil.

Of all the factors involved in the dehydration of castor oil, the effect of the catalyst is probably most important. Many hundreds of catalysts for the reaction are disclosed in the patent and technical literature. Clays, and particularly acid (10) clays or acid-activated earths (11), are known to be effective. Non-oxidizing mineral acids containing oxygen, in particular sulfuric and phosphoric acids, were first used to make mineral-soluble oils and later extended

to the drying oil process (5). Acid derivatives of sulfuric acid, especially sodium bisulfate, have been used (5). Metallic oxides (12) used for the dehydration include tungstic, molybdic, and uranic acid anhydrides. Boric acid has been claimed, as have combinations of sulfuric acid therewith (13). The dehydration has been carried out in the presence of large quantities of fatty acids, which are distilled from the mixture on the completion of the dehydration (14). Organic sulfonic acids of various types (15) have been employed. Neutral alkyl sulfates such as diethyl and dimethyl sulfate have many practical advantages (16). Many other catalysts have been mentioned or claimed to be effective.

A comprehensive study of the effect of the many possible catalysts on the properties of dehydrated castor oil and on side reactions, etc., would be a gigantic task. Forbes and Neville (17) studied the effect of many catalysts and suggested mechanisms for the dehydration in the presence of sulfuric acid derivatives and tungstic oxide (see Figure 3). It

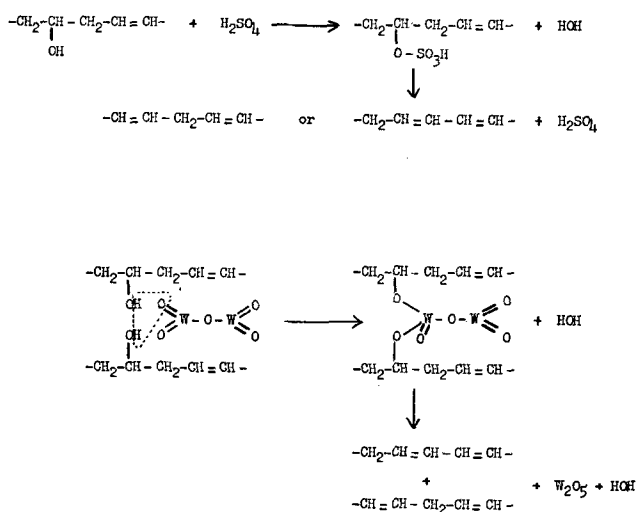


FIG. 3.

appears probable that the dehydration processes involving organic acids such as acetic (18) or fatty acids involve a mechanism similar to that for sulfuric acid derivatives, i.e., esterification of the hydroxyl group and subsequently resplitting off the acid.

Turning now to a consideration of the analytical changes which take place during dehydration, it is obviously difficult to generalize on the subject in view of the many conditions which may be employed and the complicated chemical situation which can ensue as discussed above. However, taking a set of conditions from the literature that can be considered typi-

cal, data such as that presented in Table III has been obtained. The catalyst used was 0.5% sodium acid sulfate; the dehydration was carried out under a vacuum of 22-28 inches in a 2-gallon laboratory kettle. Samples were withdrawn periodically and the constants determined. It will be noted that the acid value increased rather rapidly even though vacuum was employed. Raw castor oil is considerably higher in viscosity than are other raw oils; this is due to the "drag" or association of the hydroxyl groups on the fatty acid chains. As these hydroxyl groups are removed in the course of dehydration, the viscosity decreases. Of interest is the fact that maximum iodine value occurs at or near the point of minimum viscosity; in other words, polymerization begins to assert itself with consequent drop in iodine value, beginning at about this point. The leveling-off of hydroxyl number is also apparent (see Figure 4).

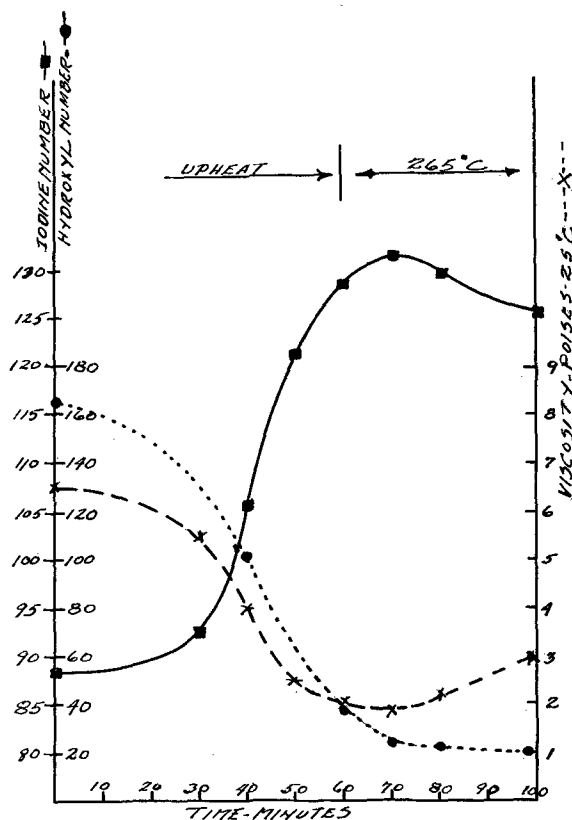


FIG. 4.

TABLE III

Time, Min.,	Temp., °C.	Acid No.	Viscosity Gardner-Holdt	Iodine No., Wijs	Hydroxyl No.
0	28	1.5	U+	87.5	166.4
30	177	....	T	92.6	.....
40	211	....	P	106.0	102.0
50	239	3.6	J	122.2	.....
60	265	....	I-	128.5	39.5
70	265	4.8	H-	132.0	26.2
80	265	....	I	129.1	23.1
100	265	5.1	L	125.6	20.1

Technologically speaking, the commercial dehydration is usually carried out in stainless, inconel, monel, or glass-lined kettles as otherwise the product is likely to be of inferior color. The kettles are generally equipped with steam jets or other vacuum source, and an agitator; they are of similar design to those ordinarily employed for alkyd resin making, etc. A diagram of a typical processing unit is shown in Figure 5. Temperatures on the order of 230-280°C. are involved, and considerable heat-input is necessitated so that Dowtherm, direct-fired, or electric heating systems are ordinarily employed. Systems for continuous dehydration have been patented (19) and described in the literature (20).

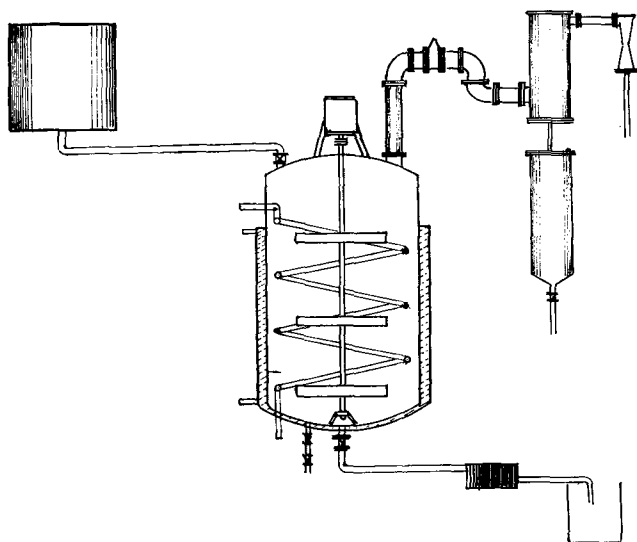


Fig. 5

One unbodied grade and several bodied grades of dehydrated castor oil are commonly recognized commercially. Most frequently used of the bodied grades is that of about Z2-Z4 viscosity. A.S.T.M. Tentative Specifications D 961-48 T for Dehydrated Castor Oil (21) (see Table IV) show the range of constants ordinarily possessed by these oils. The bodied oils are prepared in the conventional method although the temperatures employed will ordinarily be somewhat lower than those used for bodying linseed oil, since dehydrated castor oil bodies at a considerably faster rate (see Figure 6).

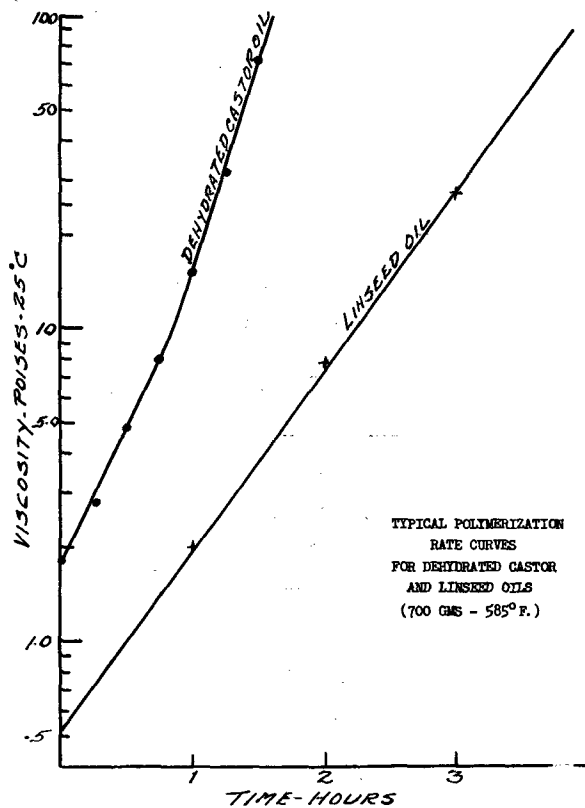


Fig. 6

TABLE IV

	Unbodied		Bodied	
	Min.	Max.	Min.	Max.
Viscosity at 25° C.....	F+	J-	Z2+	Z4-
Sp. Grav. 15.5/15.5° C.....	0.930	0.941	0.950	0.970
Acid Number.....	.....	6	.....	6
Saponification Number.....	188	194	188	194
Iodine Number (Wijs).....	130	145	100	.....
Color (Gardner 1933).....	.....	6	.....	7
Gel Time, 600° F.....	.....	145	.....	63
Set-to-touch, hrs. (0.3 Pb, .03 Co).....	.....	2.5	.....	1.4
Refractive Index, 25° C.....	1.4805	1.4825	1.4860	1.4885

By virtue of the fact that it contains no triply-unsaturated fatty acids, dehydrated castor oil has outstanding non-yellowing characteristics. As might be expected from its composition as previously discussed, many of its characteristics, i.e., drying time, alkali and water resistance, bodying rate, etc., are intermediate between those of tung and linseed oils. As might also be expected, dehydrated castor oil films alone are ultimately softer but have better flexibility than do those from linseed oil. Dehydrated castor oil, when spread in a film without added driers, yields a frosted film similar to that obtained from raw tung oil.

When used in preparing oleoresinous vehicles, the bodied dehydrated castor oils are generally employed. For example, a 25-gallon varnish using a pentaerythritol or maleic modified ester gum might be employed in interior finishes; this would ordinarily be cooked, using a bodied DCO of about Z2 viscosity. Some resins require the use of unbodied or lighter bodied DCO for dispersion. Although DCO varnishes are faster bodying than linseed varnishes, it goes without saying that they are much easier to control than tung oil varnishes. In the preparation of alkyd resins with dehydrated castor oil the unbodied grade is generally used in order that the resin can be cooked to a low acid number at higher glycerol phthalate contents; obviously the bodied grades would lead to faster gelation. Processing of DCO alkyds is carried out in the conventional manner, i.e., alcoholysis, using calcium or lead catalysts followed by reaction with phthalic anhydride. DCO alkyds are of extremely pale initial color and have excellent color retention hence are ideal for baking white enamels as previously mentioned.

Although originally developed primarily as a tung oil substitute, dehydrated castor oil now stands on its own merits so far as its uses are concerned. To mention a few, it is used in oleoresinous vehicles for interior finishes because of its excellent color retention; for the same reason and because of other specific advantages it is used in alkyd vehicles for baking white enamels, etc.; similarly, its flexibility has created uses in can coatings, etc., where this is highly desirable. Thus, dehydrated castor oil has achieved a place of its own, along with the natural drying oils, in the preparation of protective coatings.

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## Copolymerization

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COPOLYMERIZATION is undoubtedly the most active phase of present-day drying oil processing technology. It offers an infinite number of formulation possibilities even though a mass of information has already been published by a galaxy of stellar contributors. While polymerization may be

traced as far back as Berzelius, the original copolymerization has probably not been duly recorded.

Many polymers are not miscible with each other, but often their monomers may be mixed and copolymerized to a homogeneous product which combines the valuable properties of each single polymer. The drying oil copolymers, and particularly the styrenated alkyds, are excellent examples of such. In some cases a monomer will form a copolymer with another monomer which does not readily polymerize alone.



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Such copolymers have been called heteropolymers.

### Historical

To the oil chemist the simplest copolymers may be regarded as those made by the controlled copolymerization of two or more drying oils. Even these are far from simple when it comes to explaining the mechanism involved and the structures obtained. Little of value seems to have been published on the copolymerization of drying oils until the two papers of the Pittsburgh Club (59) on soya-tung oil combinations. From the practical sense the scope of such oil copolymers is still somewhat limited for, after all, the resulting product is still an unmodified oil. From time immemorial the varnish maker in a practical way has been copolymerizing oils in the presence of hard gums to increase hardness, toughness, and drying speed. Regardless of type, these varnish gums are in general effective principally because they allow the larger copolymer sizes to form but keep them in a soluble and therefore usable condition for forming coatings. The limitations of copolymerizing oils in the presence of a soluble resinous polymer are obvious. The new developments in coating compositions have been achieved through the actual tie-up of small monomeric units to unsaturated centers of oils. Many of the most useful monomeric units form polymers which are either incompatible with bodied drying oils

or do not show any particular advantage if they are compatible.

The first attempt of prime importance to improve upon varnishes, the first important type of drying oil copolymer, was the development of the well known oil-modified alkyds. In a sense the drying oil alkyds are copolymeric systems and truly so in accordance with the Carothers' (9) concepts because the oil polymer is actually and effectively tied to the polyhydric alcohol-polybasic acid polymer. The segments of both monomers are present in the chains, but the system is heterogeneous in the sense that part of the copolymer is made up of polymerization units arising from unsaturation and part from units of condensation-polymerization. When the oil acid portion of alkyds is non-drying, it is not more than a polyester complex, but when semi-drying or drying acids are involved, then the alkyd bears a definite relationship to copolymers. Bradley (7) distinguishes between "addition" copolymers and "esterification" copolymers. The alkyds will be discussed on this program in another paper and are being mentioned merely to indicate the relationship. This paper discusses principally "addition" copolymers resulting from unsaturates and poly-unsaturates, in which a substantial proportion of the composition is a drying oil and/or fatty acids. Some glimpses are given of new, competing copolymers which are commercially available today that contain little or no drying oil and constitute a definite threat to compositions hitherto based largely on vegetable oils.

Styrene, on account of its potential low cost and great availability, has received the most attention as a copolymer-forming ingredient. As early as 1931 I. G. Farbenindustrie A. G. (35) disclosed emulsion polymerization of styrene with a drying oil using hydrogen peroxide catalyst. This was the first styrene-oil copolymer unless Kronstein's (45) styrene-tung oil composition of 1909 could have been one. In 1934 Lawson and Sandborn (47) described preparations involving the copolymerization of styrene and a drying oil in the presence of rosin and an inert solvent, using a peroxide catalyst.

Stoesser and Gabel (76) in 1940 copolymerized tung oil and styrene but claimed products only with 5% or less of oil since they were aiming at toughening the plastic rather than improving the oil. In the same year came Flint and Rothrock's (20) disclosure claiming an interpolymer of styrene formed by heating the monomer in the presence of solvent with a preformed frosting oleoresinous varnish base. Ellis (18) also disclosed a composition based on a styrene copolymer of a drying oil varnish base made by sol-