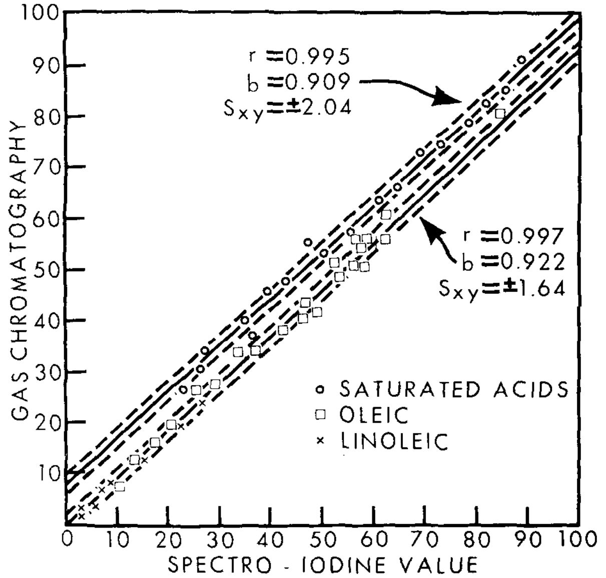

FIG. 9. Comparison of data by gas chromatographic and spectro-iodine value procedures.

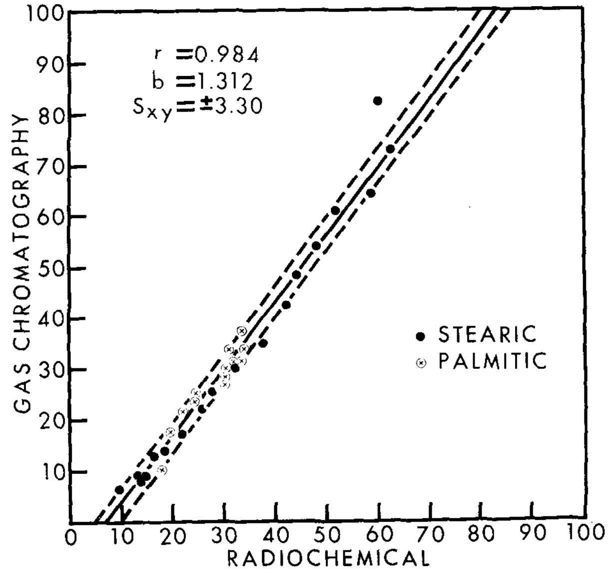

FIG. 10. Comparison of data by gas chromatographic and double-label isotopic dilution procedures.

determinations, b) gas chromatography, and c) differential counting of tritium and C^{14} radioactivity by using a liquid scintillation spectrometer. A comparison of the results of fatty acid determination by these three methods is summarized in Figure 9, where spectro-iodine value determinations are plotted against gas chromatographic values, and in Figure 10 where radiochemical analyses are plotted against gas chromatographic values.

Aside from observing the close correlation and low error of these independent methods, it should be recorded that spectro-iodine values required over a month to perform; gas chromatographic determinations, weeks; and radiochemical analyses, only hours. Perhaps more remarkable is the fact that none of these analytical methods were available to the research chemist a decade ago. In the field of lipid research it is hoped these or other unmentioned advances in technique will bring future advances in scientific knowledge of fats, including drying oils.

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Dehydrated Castor Oil

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DEHYDRATED castor oil is a synthetic drying oil prepared from castor oil, a nondrying, natural vegetable oil. Since the availability and cost of dehydrated castor oil depends on castor oil, a short summary of its source, use, and composition seems appropriate.

Castor Oil

The castor plant grows widely in the tropical and near-tropical regions of the world as a perennial and is cultivated in the temperate zones as an annual. About one billion pounds of beans per year are processed, which yield about 500 million pounds of oil. The principal producing-areas are in Brazil and India. About 125 million pounds of castor oil were used in the United States during 1958.

One hundred years ago castor oil was obtained from castor beans grown in the United States. At the beginning of the 20th century increasing quantities of beans were imported until, shortly after World War I, all oil used in this country was obtained from imported beans. Beginning in 1950, oil began to be imported as well as beans. The dependence on foreign sources has resulted in shortages and wide fluctuations in price. It had been recognized for some time that domestic production of the bean was desirable to assure a supply of this critical commodity in case of a natural emergency as well as a stable price to foster development of new products and uses from castor oil as the raw material. While previous studies had been conducted, in 1948 a concentrated effort by the government and private industry started to reestablish castor as a domestic crop.

The current success of this program is indicated by noting that 1,800,000 lbs. of castor oil were obtained from domestic seed grown in 1956, 10,000,000 in 1957; 22,000,000 will be produced from seed grown this past year. While this is still only 15% of our current consumption, the trend is significant. It is already having a stabilizing influence on the price of castor oil, which is reflected in the supply and price of dehydrated castor oil. While there is still work to be done, the agronomists and engineers have done a fine job in breeding new castor varieties to reduce the size, decrease seed shattering, and develop appropriate harvesting machinery. In 1958 the average yield of seed, expressed as castor-oil equivalent, from one acre of land was about 1,000 lbs. While most of the crop was on irrigated land, it is of interest to note that this is about five times as much oil as from an average acre of flax or soybeans.

Castor oil occupies a unique position in the field of natural fats and oils. While, like other common vegetable oils, it is a triglyceride, it is unusual in that the acid components are predominantly a hydroxy compound, also called ricinoleic acid. There is still some minor disagreement among authorities as to the exact fatty acid composition of the oil. However the following proportions of mixed acids are tentatively accepted:

Ricinoleic acid	90%
Linoleic acid	3%
Oleic acid	4%
Saturated acids	3%

In the preparation of dehydrated castor oil, we shall be concerned only with the chemistry of the ricinoleate portion. The other acid components remain essentially unaltered.

Castor oil and its chemical derivatives are used by many industries and in a large number of products. A recent U.S.D.A. circular (1) states the total apparent disappearance of castor oil in the United States in 1958 to be 120 million pounds. It breaks down the consumption as soap less than ½ million pounds, drying oil products 47 million, miscellaneous products 33 million, and unreported, including government stockpiling, as 39 million. In a paper presented before the Chemurgic Council in April, 1959, we estimated the 1958 consumption to be 125 million pounds as used in the following class of products:

	Proportion	Million pounds
Protective coatings	45%	56
Plastics and plasticizers	19%	24
Lubricants	13%	17
Surfactants	7%	9
Hydraulic fluids	5%	6
Cosmetics and pharmaceuticals	2%	2
Miscellaneous	9%	11
	100%	125

No discussion on the use of castor oil is complete unless it is explicitly pointed out that the medicinal use that made castor oil famous, even though still important, accounts for a very minor portion of its consumption, probably about 1%. The importance of protective coatings in the utilization of castor oil is obvious from the above table. The production of dehydrated castor oil for use in paints and varnishes is the largest single use for castor oil. It is estimated that in 1958 this was about 50 million pounds. There are a number of miscellaneous uses for castor products such as paint additives, emulsifying agents, etc., that account for the estimated remaining 16 million pounds consumed. In a study by Stanford Research Institute economists (2) it was estimated 64 million pounds were used in paints, varnishes, and resins. It was predicted this usage would increase to 112 million in 1965.

Dehydration of Castor Oil

Dehydrated castor oil is prepared by the removal of the hydroxyl group and an adjacent hydrogen atom from ricinoleic acid chain as water to form octadecadienoic acid chain, with the double bonds at the 9,12-positions or at the 9,11-positions. The conversion results in 2–3 parts of nonconjugated groups to each one part of conjugated group.

Sixty years ago it was known that drying properties could be developed in castor oil by heating. However the principal interest in castor oil was then in its use as a lubricant. Thus development work on dehydration was directed towards making castor oil soluble in mineral oils. In 1913 Rassow (3) showed that the product obtained from heating castor oil in the presence of acid catalysts had increased unsaturation. Fokin (4, 5) identified the products as conjugated and nonconjugated fatty acids similar to those obtained from linseed and tung. Apparently the practical aspects of these observations were not realized until Scheiber (6) in 1928 announced his "discovery" of his method for making a drying oil from castor oil. Scheiber's process started with the castor oil fatty acids, technical ricinoleic acids, which were obtained from the oil by hydrolysis. These acids were destructively distilled to give the linoleic acids. By reesterification with glycerol, dehydrated castor oil was formed, known as "Scheiber Oil." While his process would be considered impractical under current conditions, it was of interest in Germany at that time because of the acute shortage of tung oil. Furthermore it served to call attention to the desirable properties of dehydrated castor oil for protective coatings. Shortly after Scheiber's disclosures, methods for catalytically processing the oil were developed. Ufer (7, 8) is usually given credit for the first practical process. Dehydrated castor oil became a commercial product in this country in 1936.

Commercial dehydration is carried out in large stainless steel kettles, which are equipped with an agitator and steam jets for vacuum. The catalyst is added either before heating or when the oil reaches temperature. It is heated with Dowtherm, direct-fired, or electric to 250°–300°C. under a vacuum to pull off the water which is formed. Systems for continuous dehydration have been patented (9), described (10), and are in use. The catalysts generally used are of an acidic nature, such as potassium and sodium acid sulfates, sulfuric acid, phosphoric acid, phthalic anhydride, acid earth, tungstic oxide, organic sulfonic acids, etc. The technical and particularly the patent literature on catalysts used is very extensive. Forbes and Neville (11) suggested mechanisms for the reaction. It involves a complex formation with the hydroxyl with subsequent splitting off under the influence of heat and regeneration of the catalyst.

R. L. Terrill (12), in his excellent paper given before the 1950 Short Course on Drying Oils, presented the following data (Table I) on a laboratory preparation of dehydrated castor oil. While details of commercial procedures may not be disclosed, this is reasonably typical. "The catalyst used was 0.5% sodium acid sulfate; the dehydration was carried out under a vacuum of 22–28 in. in a 2-gal. laboratory kettle. Samples were withdrawn periodically and the constants determined."

TABLE I

Time	Temp.	Acid No.	Viscosity G.H.	Iodine No.	Hydroxyl No.
(min.)	*(°C.)*				
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

The Gardner-Holdt viscosity of raw castor oil is about U while that of the other common vegetable oils, such as raw linseed or soybean, is about A. This high viscosity results from the hydrogen bonding effect of the hydroxyl group. Table I shows that the viscosity reaches a minimum at the point where the iodine value is a maximum, which in the case cited is after 70 min. After this time there is some further "dehydration" while the iodine number decreases and the viscosity increases because of polymerization. Continued heating would give the bodied dehydrated castor of commerce. That most frequently used has a viscosity of Z3. The unbodied dehydrated castor oil of commerce is usually that taken at the minimum viscosity.

Composition of DCO

There is a tendency in the protective-coating industry to abbreviate dehydrated castor oil to "castor oil." This is confusing since raw castor oil sometimes is used in protective coatings as a plasticizer, in the preparation of resins, etc. If dehydrated castor oil must be abbreviated, "DCO" is suggested.

There are a number of complicating factors in the dehydration of castor oil that affect the composition of the product and its properties. These are listed and briefly discussed: degree of conjugation, residual hydroxyl value, *cis-trans* isomerism, double-bond shift, estolide formation, polymerization, hydrolysis, and color formation.

In the equations given above for the preparation of dehydrated castor oil it was indicated that two products were formed, a nonconjugated 9,12-octadecadienoic acid chain and a conjugated 9,11-octadecadienoic acid chain. The relative amount of each has been the subject of considerable discussion during the past 20 years. Scheiber, in his original work, assumed that about 90% of the acids formed were conjugated. This was based principally on the observation that the Wijs iodine value increased upon prolonged reagent contact. Shortly thereafter Boeseken and Hoevers (13) studied the reaction of dehydrated castor oil derivatives with maleic anhydride. It was assumed that only the conjugated portion of the DCO products would react. From these results it was reported the conjugated double bonds in the mixture were approximately 75%. In 1940 Priest and Von Mikusch (14) published a comprehensive review of earlier work and their experimental studies which, based on a modified diene value, indicated a conjugated content of 17.3 to 25.4% (*i.e.*, the 9,11 isomer in the glyceride). Later studies on the maleic anhydride reaction indicated that it is not complete since the *cis* and *trans* isomers react differently. There are indications that the *trans*-conjugated double bonds add maleic anhydride more easily than the *cis-trans* or *trans-cis* isomers and that the *cis-cis* compounds may not react at all or possibly only after a change in configuration. Various halogen-addition methods were also used in an attempt to determine the percentage of conjugation, but their quantitative results were subject to considerable uncertainty. Probably the best method for measuring this property is by the more recently developed spectrophotometric method. In 1955 A.S.T.M. published a method for the spectrophotometric diene value of dehydrated castor oil and its derivatives (D1358–55T). Using this method, commercial unbodied dehydrated castor oil was found to have about a 25% conjugation while the distilled acids had about 32%. When dehydrated castor oil is heat-bodied, additional conjugated bonds are formed, which are usually masked by the more rapid removal by polymerization. However Chowdhury and Mukerji (15) stated that if dehydrated castor is maintained at a temperature of 200°C. for 90 min., the conjugated isomer is observed to increase by 3.6%.

Assuming that 25–30% conjugation is obtained, a satisfactory explanation seems to be lacking for this low value. The free energy content of a conjugated system is lower than that of a nonconjugated. For this reason, assuming free competition for the hydrogen on either side of the hydroxyl, there should be more conjugated than nonconjugated material present. This poses an interesting study that might have important practical applications.

As castor oil is dehydrated, the hydroxyl value decreases and should be reduced to 0 when the oil has been completely dehydrated. Actually, under even the most severe dehydrating conditions, an oil with a hydroxyl value of 0 has not been observed. It is believed doubtful that the hydroxyl value actually measures the residual castor oil but probably results from the formation of some mono- and diglycerides as well as the dihydroxystearic acid which is known to be originally present in the raw castor oil. For these reasons hydroxyl value is not often used as an indication of the quality of dehydrated castor oil or its fatty acids.

The double bond in the 9–10 position of castor oil, like most natural oils, is of *cis* configuration. Under the usual methods of dehydration it is believed to remain unchanged. Thus we would obtain the following isomeric linoleic acids:

9 *cis*, 11 *trans*-octadecadienoic
9 *cis*, 11 *cis*-octadecadienoic
9 *cis*, 12 *trans*-octadecadienoic
9 *cis*, 12 *cis*-octadecadienoic

There are indications that all of these isomers are formed, but apparently the relative proportion of the *cis-trans* to *cis-cis* is not known. It should be possible to determine this ratio by modern isolation and infrared techniques. For lack of better data, it may be assumed that the ratio of *cis-trans* to *cis-cis* in both the conjugated and nonconjugated octadecadienoic chain is 1:1. Studies of other oils have indicated that the *cis* and *trans* double bonds have different rates of oxidation and polymerization. Thus we may expect the stereo isomers to have their effect on the properties of castor oil, and it has been speculated that the aftertack sometimes observed as well as the good film flexibility may be caused by the uneven oxidation of these isomers.

We have previously indicated that the *cis* 9-10 double bond remains intact during the dehydration. However von Mikusch (16) states that some 8,10-octadecadienoic acid is formed during the dehydration of castor oil. It is not surprising that some double-bond shifting would occur although it is believed to be slight, and it is doubtful that it would affect appreciably the properties of the dehydrated castor oil.

It has been known for some time that when ricinoleic acid is stored or heated, estolides (sometimes called polyricinoleates) are formed. These result from the reaction of the hydroxyl group with the carboxyl group of ricinoleic acid, splitting off water and forming an ester group. When the hydroxyl group and carboxyl group are from the same acid, a lactone is formed. When two ricinoleic acids are involved, a hydroxyl group from one and the carboxyl from the other, a simple dimer results. If the dimer continues to react with itself, using the residual hydroxyl and carboxyl groups, a lactide is formed. On the other hand, if the dimer reacts with other ricinoleic acids either through the hydroxyl or the carboxyl, linear polyesters are built up. Obviously these may eventually react within the long-chain molecule to form cyclic polyesters. In the formation of estolides it is believed that all of these types of reactions take place with short-chain linear polyesters as the predominant reaction. In the original Scheiber reaction the dehydration of the acids is a decomposition of the estolides rather than a simple splitting off of water as previously indicated. In fact, a variation of the dehydration process involves esterification of the hydroxyl with fatty acid or acetic acid before the decomposition by heat. Estolide formation may also occur in the oil by ester interchange under the influence of heat and catalyst. The hydroxyl group in the ricinoleic chain may substitute in the glyceride ester group, making a diglyceride. This may be one of the reactions accounting for the hydroxyl value of the resulting product. It is possible that this reaction may continue and actually liberate glycerine. There is evidence for this reaction in the observed acrolein formation during the dehydration of castor oil. Estolides have also been formed during the heating of methyl ricinoleate with an alkali catalyst and liberation of methyl alcohol. Some idea of the amount of estolide formation can be obtained by observing the optical activity of dehydrated castor oil. The writer has observed that castor oil has a specific rotation of 5.24 (17). When the hydroxyl group is esterified, there is about a five-fold increase in optical activity. Two samples of unbodied dehydrated castor oil were observed to have 4.94 and 5.05 specific rotation, respectively. While the indicated value might be about 15–20%, some caution should be used in the interpretation since we do not know the optical rotation of a pure estolide. However the results do indicate that considerable estolide material is present. During heat bodying the estolides apparently break down since the bodied dehydrated castor oil has been observed to be 1.26.

The nonconjugated and particularly the conjugated unsaturated components that are formed during dehydration will heat-polymerize. Since the temperature of dehydration is in the same range that is used for the heat polymerization of oils, it is not surprising that the resulting product contains polymerized material. If an unbodied dehydrated castor oil is desired, polymerization is minimized by use of a shorter time and as low a temperature as possible. The lowest viscosity oil has a Gardner-Holdt value of about G. This increase in viscosity over A, which one might expect for a glyceride oil containing no polymerization, is caused both by the estolide formation (ester linkages) as well as heat polymerization (C—C linkages). What proportion of body increase is attributable to each of these factors is not known. In any case this mild viscosity increase might be considered an advantage since it is a first step in the formation of film.

During the dehydration of castor oil there is frequently a small amount of moisture present and an acid catalyst. Thus considerable care must be used in the manufacture to prevent hydrolysis. It is now possible to control conditions so that the better commercial dehydrated castor oils have an acid value of only about 4, indicating less than 2% hydrolysis.

Another indication of skill in manufacture is the color. A good grade of raw castor oil is nearly water-white. However the drastic treatment it undergoes during dehydration would tend to darken the oil. By rigorously controlling the conditions of manufacture, the unbodied commercial castor oils should be lighter than a color of 6 and are often in the Gardner-Holdt 4 range. Thus they are among the lightest oils used in protective-coating technology. Since DCO does not contain any fatty acid with three double bonds, it does not yellow on exposure in a film and retains its good color whether used as an oil or in an alkyd.

The American Society for Testing Materials has agreed on specifications (D 961-55T) for dehydrated castor oil, which are given in Table II.

TABLE II

	Unbodied	Bodied
Viscosity at 25°C	F to I	Z2 to Z4
Specific gravity, 25/25°C	0.926 to 0.937	0.944 to 0.966
Acid number	6	6
Saponification number	188 to 195	188 to 195
Iodine number (Wijs)	125 to 145	100
Color No. (Gardner 1933)	6	7
Gel time at 600°F., min	145	63
Set-to-touch time, hr	2.5	1.4
Refractive index at 25°C	1.4805 to 1.4825	1.4860 to 1.4890

Utilization of DCO

In the previous discussion we have attempted to give a picture of the chemical composition of dehydrated castor oil. However the real value of the oil is determined by its properties when used. In other words, "the proof of the pudding is in the eating." DCO was originally developed as a tung oil substitute. Unfortunately this thought still prevails to some extent. Actually DCO should be considered a unique drying oil that is different from tung, linseed, soya, oiticica, etc. When substituted for other drying oils, it is usually desirable also to modify the processing procedure to obtain optimum use of its properties. If it is necessary to classify DCO in relation to the other drying oils, it could be considered intermediate between linseed and tung. The principal advantages that DCO imparts to protective coatings are good flexibility, tough dry, and good retention of color and gloss. In processing, it has rapid but controllable heat-bodying characteristics.

Aftertack (residual tack) has been cited as a deficiency in dehydrated castor oil varnishes. This effect was most noticeable in the earlier oils that were incompletely dehydrated. Also, since DCO was originally developed as a tung oil replacement, it was substituted directly for tung oil in the formulations without changing the processing conditions. While modern technology has minimized aftertack of DCO as a problem, it is sometimes encountered and warrants further discussion. The tendency for DCO toward aftertack probably results from its mixed isomeric (*trans* and *cis*) structure and/or its estolide content. It may be measured by pressing a 90-lb. Kraft paper on the surface of the film with a force of 2 p.s.i. for 5 seconds. Ten seconds are then allowed for the paper to release of its own weight when the panel is inverted. If the paper releases in this time, aftertack is considered absent. Patton (18) suggests several ways for overcoming any residual tack in varnish vehicles.

1. Use a good grade of DCO oil.
2. Shorten the oil length of the varnish.
3. Use bodied DCO with modified phenolic resins and unbodied DCO with 100% phenolic resins.
4. Use a bisphenol phenolic resin as a partial or complete replacement for any phenolic resin causing trouble.
5. Substitute a maleic resin for a portion of the phenolic resin.
6. Substitute a small amount of tung oil (about 20%) for a portion of the DCO.

The utilization of bodied dehydrated castor oil can be exemplified by the preparation of a furniture varnish. This type of varnish should have a fast dry, good appearance, and low cost together with hardness and durability. One hundred pounds of a bisphenol modified phenolic resin (Arochem 335—U.S.I.) are added to 6½ gal. of boiled DCO (Castung 403-Z3—Baker Castor Oil Company) heated to 585°F. and held for a clear pill. It is thinned with mineral spirits to a 50% nonvolatile and 0.5% lead and .05% cobalt (nonvolatile basis) driers added. The resulting varnish should have a viscosity of E and Gardner color of 11. It should set-to-touch in 14 min., dry hard in one hour, and be tack-free in six.

A medium oil-length alkyd made by using unbodied DCO is a multi-purpose resin. As a baking alkyd it exhibits fast baking speed, good adhesion, flexibility, color, and good gloss-retention. It can be used alone or as a plasticizer in conjuction with urea or melamine resins. As an air-dry alkyd its satisfactory drying and film properties indicate its use on machinery, metal containers, and signs and for metal decorative purposes in general. In the formulation given below, a small amount of soybean oil is added to control the viscosity during the cook and reduce the tendency to gas-check.

Medium Oil-Length DCO Alkyd
(55% oil, 32% phthalic anhydride)

	Parts (by weight)
Unbodied DCO	49.5
Soybean oil	5.5
Phthalic anhydride	34.8
Glycerine (100%)	14.5
	104.3
	4.3
Water evolved	100.0

The two oils and 10.5 parts of the glycerine are heated with an ester interchange catalyst (0.6% lithium ricinoleate) to 450°F. and held for 45 min. with sparging, which is maintained throughout the cook. Next the phthalic anhydride and the remaining glycerine are added, and the mixture is heated to 490°F. It is held at that temperature (four hours for a laboratory cook) until a 50% mineral spirit solution has a viscosity of Z1. The mineral spirit viscosity will reach about Z3 on cooling and the acid value of the resin about 8.

Both Patton (19) and Terrill (20) have shown DCO to have merit in the preparation of outside house paints. Vehicles containing both bodied and unbodied DCO are more efficient as a grinding medium than the linseed counterparts. They usually exhibit a faster dry. In general, the long-range performance and durability of 100% DCO white house paints appear equivalent to linseed oil paints while in the case of self-primed paint systems a slight advantage in durability has been noted. The use of DCO in house paints has been retarded in the past by its high price. Also the newness of DCO as a drying oil and the long testing period required (four to five years) for an adequate evaluation make acceptance slow. Now with a better stabilized price structure on castor oil, additional consideration should be given to the use of this unique drying oil in outside paints.

Since the use of tall oil in alkyds is being discussed in this Drying Oil Symposium, it would seem of interest to point out the advantage of blending with DCO. While there are deficiencies in tall oil alkyds, they are attractive from cost considerations. It has been observed that a blend of tall oil with unbodied dehydrated castor oil to give an approximate 30% oil modification can be used to make a flat alkyd with excellent application properties. The DCO imparts improved flexibility to the film, permits dilution without undue loss of viscosity, improves hold-out, and eliminates "brush drag." The preparation and properties of a variety of varnishes made with tall oil-DCO blends are given in an article by Patton and Lindlaw (21).

DCO Fatty Acids

Dehydrated castor oil fatty acids may be prepared in several ways. As previously pointed out, Scheiber's original preparation of the oil was from DCO acids prepared by destructive distillation of castor oil fatty acids. An improvement in the preparation from castor oil acids is suggested by Rowe (22). It consists of esterifying the secondary hydroxyl group of ricinoleic acid with the DCO acids obtained in a previous batch. Under the influence of heat the DCO acid is split off with the removal of an adjacent hydrogen to form an additional DCO acid. In actuality a mixture of conjugated and nonconjugated acids would be used for esterification and obtained by the reaction. Also some estolide formation could not be avoided.

DCO acids may also be prepared by saponifying and splitting DCO. This is at present the preferred method for commercially preparing the acids. The better grades are further refined by distillation.

A good grade of DCO acids contains about the same mixture of linoleic isomers (*cis* and *trans*, conjugated and nonconjugated) discussed under the oil except that there are probably fewer estolides present. Since castor oil is 90% ricinoleic plus a small amount of natural linoleic, the resultant DCO acids would be very nearly pure linoleic acids. Spectrophotometric diene values indicate that the acids have a slightly higher percentage of the conjugated isomer.

A.S.T.M. has recently issued the following tentative specifications for dehydrated castor acids (D-1539-58T):

	Type I	Type II
Acid value	195–200	187–195
Saponification value	195–200	193–199
Iodine value	150–156	138–143
Color (Gardner)	1 max.	5–8
Spectrophotometric diene value	28–35	25–32

Type I is the distilled DCO acids, and Type II is undistilled.

The characteristic feature of the top grade DCO fatty acids is that they are composed almost entirely of dienoic acids, accompanied by negligible amounts of nondrying acids and no acids with three double bonds. Thus excellent drying alkyds with little yellowing tendency may be prepared. No aftertack has been observed in the alkyds made with the acids. Since the acids are more expensive than the oil, they are used principally when some special property is desired. The less expensive undistilled acids may be used where darker color and slower bodying characteristics are permitted.

DCO acids are used to modify epoxy resins (reaction products of epichlorohydrin and bisphenol). The epoxy resin functions as a high-molecular-weight polyalcohol which esterifies the fatty acids to form esters. As an example of the preparation of these esters, 60 parts of epoxy resin (Epon 1004, Shell) and 40 parts of DCO Acids 9–11 Acids, The Baker Castor Oil Company) are cooked in an inert gas at 500°F. to an acid number of 2. It is thinned to 50% solids with xylene. 0.04% cobalt is added for air-dry and 0.005% cobalt for baking. It is designed especially for use with urea or melamine resins in the formulation of low-bake metal finishes. In air-dry applications, while not suitable for brushing, it may be sprayed or dipped and will reach the tack-free state in 2–3 hrs. The principal purpose of the fatty acid modification is to produce the desired flexibility without lessening the excellent properties imparted by the heat-converted epoxy resin. Undistilled DCO acids are sometimes used because of the price advantage and faster esterification rate. However the distilled acids are preferred for good color, maximum baking speed, and optimum chemical resistance and toughness.

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Copolymer Drying Oils

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THE COPOLYMER drying oils grew out of the discovery that vegetable oils could be modified with natural resins, resulting in improved properties. The discovery must have been greeted with cheers by early formulators. Drying oils were despairingly slow in drying and were soft. The natural hard resins, used alone, were entirely too brittle to be practical. It was a happy chance that resulted in a compromise of many good properties of both oil and resin by the simple expedient of heating to induce compatibility. As the demand for oil-modified resins increased, synthetic resins were substituted for the natural because of the latter's limited supplies and erratic quality. Oil-modified phenolics and alkyds were the result.

The uses for oil-modified resins became diverse, and requirements became more severe. The market demanded lower cost, improved color, and faster drying. These needs could be met by modifying oil-alkyd systems with vinyl monomers. Indeed it was later found that the oil itself could often be successfully modified with the vinyl monomer alone, and the vehicle resulting from such modification fits the title, a copolymer drying oil.

Preparation of the Copolymer Oil. For purposes of