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A. E. RHEINECK
SYNTHETIC HARD RESINS PREPARED FROM α, β -UNSATURATED
POLYCARBOXYLIC ACIDS

2,569,495

Filed Sept. 9, 1950

2 Sheets-Sheet 1

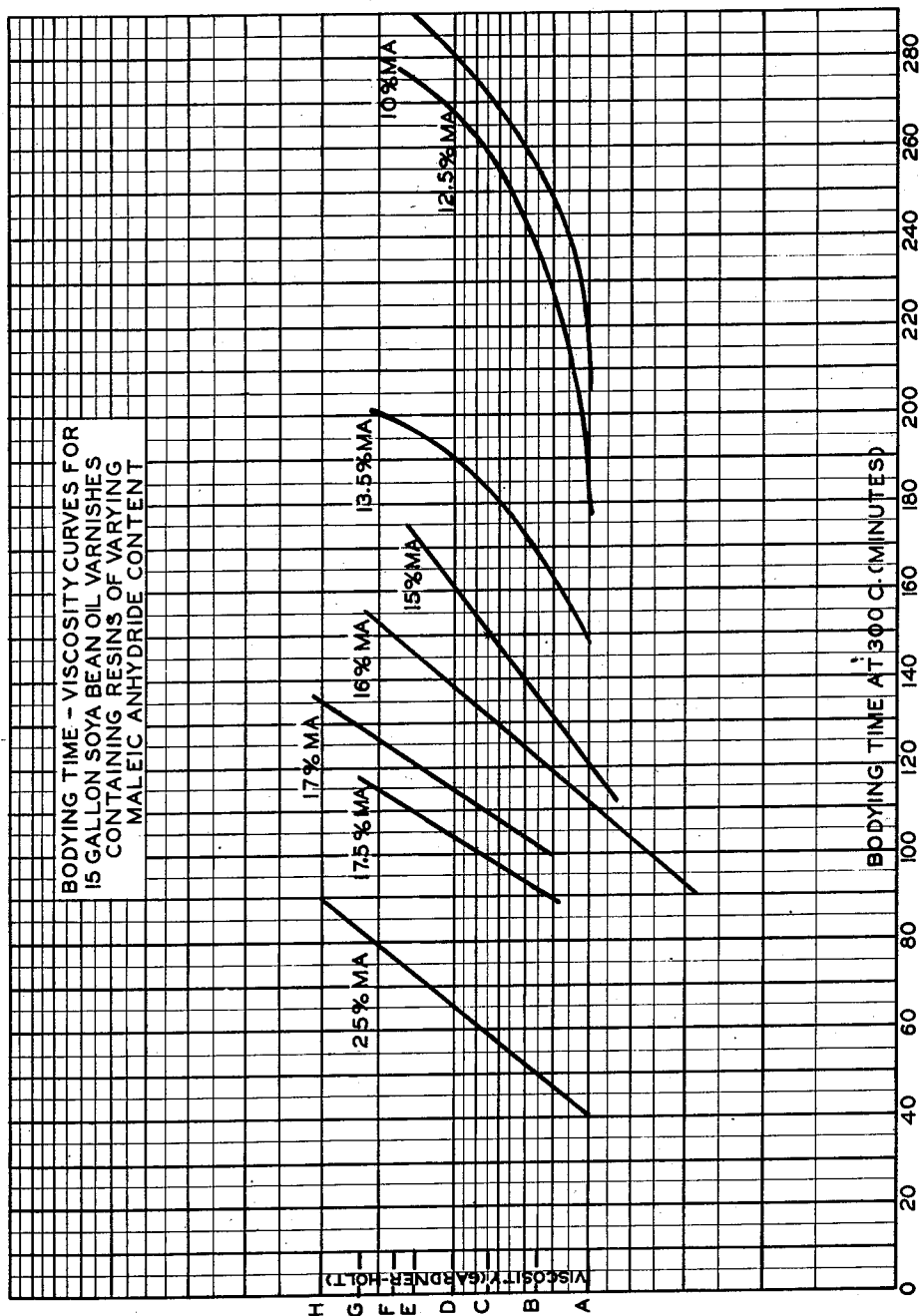


FIG. 1

ALFRED E. RHEINECK.
INVENTOR.

BY

Ernest G. Peterson

AGENT.

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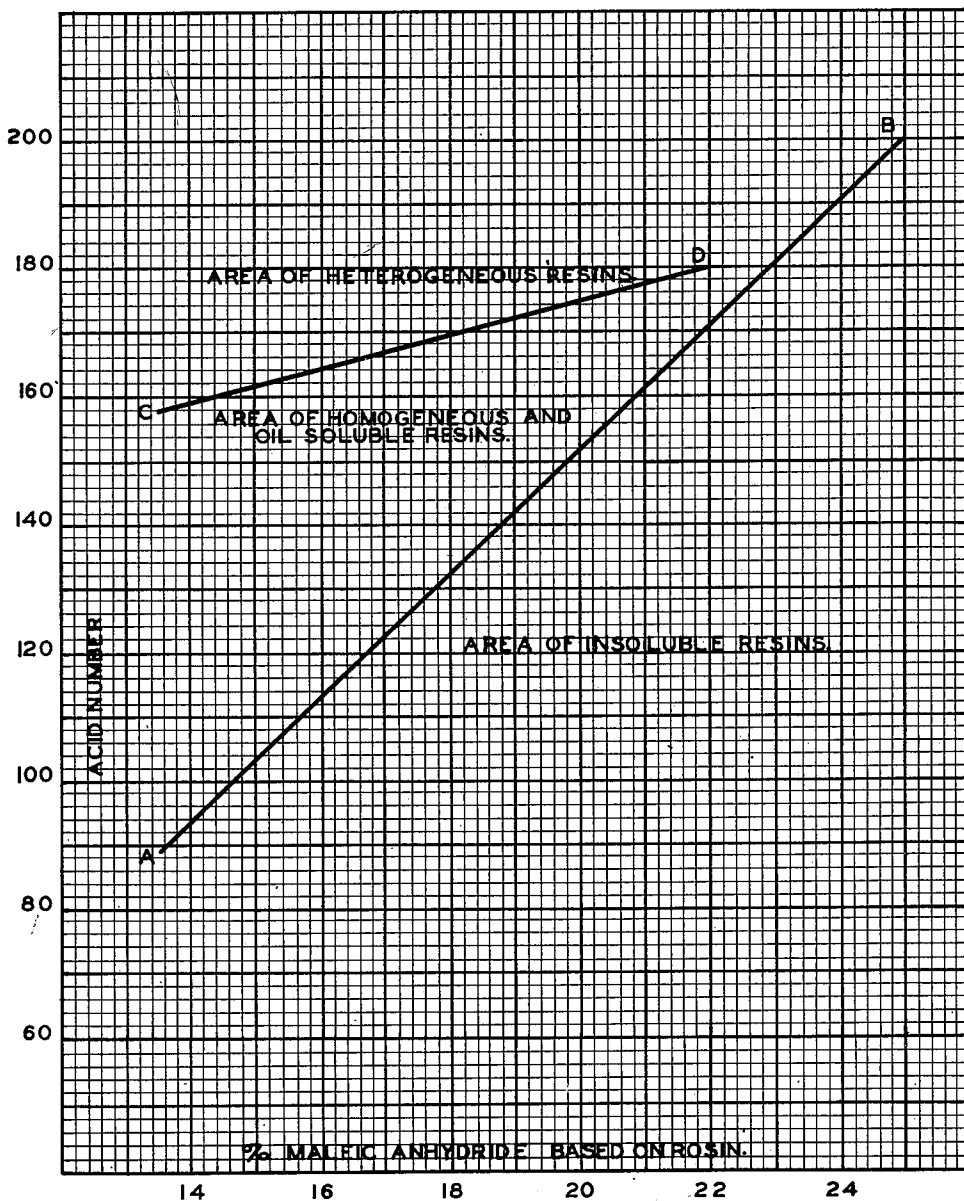


FIG. 2

ALFRED E. RHEINECK.
INVENTOR.

BY

Ernest G. Peterson

AGENT.

UNITED STATES PATENT OFFICE

2,569,495

SYNTHETIC HARD RESINS PREPARED
FROM α,β -UNSATURATED POLYCARBOXYLIC ACIDSAlfred E. Rheineck, Wilmington, Del., assignor to
Hercules Powder Company, Wilmington, Del.,
a corporation of Delaware

Application September 9, 1950, Serial No. 183,983

15 Claims. (Cl. 260—26)

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This invention relates to hard varnish resins derived from a pentaerythritol, an α,β -unsaturated polycarboxylic acid or anhydride and a rosin acid and to methods for the production thereof. More particularly, it relates to such resins that are suitable for cooking with unbodied oils, especially soybean oil and the like, to provide oleoresinous varnishes and to methods for the production of such resins.

It is well known that maleated glycerol esters of rosin may be cooked with drying oils to provide desirable oleoresinous varnishes. In this connection reference is made to U. S. 2,063,542 to Carleton Ellis and U. S. 2,039,243 to Hans Krzikalla. Similarly, maleated pentaerythritol esters of rosin may be employed for this use. The latter type esters and their utility in the oleoresinous varnish field are disclosed in U. S. 2,322,197 to F. G. Oswald and U. S. 2,344,194 to G. R. Anderson.

The drying oils which are used in the manufacture of oleoresinous varnishes are of two types—the so-called "hard" oils exemplified by tung oil and oiticica oil and the so-called "soft" oils exemplified by linseed oil, fish oil, dehydrated castor oil, safflower oil, and soybean oil. Generally, the soft oils require maleic-modified rosin esters to produce acceptable varnishes as contrasted with the hard oils which require only simple rosin esters or ester gums. Secondly, in order to process these soft oils into acceptable varnishes, they are usually prebodied to shorten the varnish cooking cycle. Accordingly, by using the prior art maleated rosin esters and by prebodying the drying oil, it has been possible to produce very desirable and commercially acceptable varnishes from linseed oil, fish oil, dehydrated castor oil, etc. This technique has not, however, provided an acceptable oleoresinous varnish in the case of the less unsaturated oils such as soybean oil and safflower oil. With soybean oil, the varnish cooking cycle required to provide a varnish of acceptable body, drying speed, etc., is so long that the resulting varnish is extremely dark in color. Extremely dark oleoresinous varnishes are of limited utility per se, and they are furthermore of no utility in formulating white and light-colored protective coatings. Hence, as a practical matter, soybean oil, which is now available in large supply and at low cost, has been almost excluded from this art. Safflower oil occupies substantially the same position as soybean oil in this respect.

I have now discovered a hard resin which is unusual in that it can be used successfully with

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the less unsaturated oils, i. e., safflower and soybean oils. Any grade and type of these oils can be used, namely, unbodied oils as crude, raw, break-free, and alkali-refined, as well as bodied oils. When any of these oils are used with the resin of this invention, varnishes with relatively short cooking cycles, acceptable body, drying speed, etc., result. Since the varnish cooking cycles are short, the varnishes are light in color and, hence, they can be used for the same purposes as oleoresinous varnishes prepared from the above-mentioned maleic-modified rosin esters and soft oils such as linseed oil, dehydrated castor oil, etc. This new resin is not, however, necessarily limited to cooking with soybean and safflower oils. Desirable varnishes can also be made with other soft oils such as dehydrated castor oil, linseed oil, and fish oil. Also, treated oils such as maleic-treated soft oils and cyclopentadiene-treated soft oils (cyclopentadiene copolymer oils) may be cooked with the resins of this invention to provide desirable varnishes.

The new resins to which I refer are hard resinous esters of a pentaerythritol and an adduct of a rosin acid material and an α,β -unsaturated polycarboxylic acid or anhydride. The adduct involved in the ester is one having an unusually high content of α,β -unsaturated polycarboxylic acid as compared with prior art practice for this type of resin. The amount of α,β -unsaturated polycarboxylic acid employed in the adduct must be from 0.46 to 0.86 mol per mol of the rosin acid. This range is critical with respect to obtaining resins having the desirable properties hereinabove discussed.

The ester resins have unusually high acid numbers. Stated broadly, it is required that the esters have an acid number which is low enough to provide an ester which is substantially clear but which at the same time is not below line AB of Fig. 2 hereof. The range of operable acid numbers varies with the mol ratio of α,β -unsaturated polycarboxylic acid to rosin acid as will be seen by an inspection of Fig. 2. These acid number ranges are critical as it is only within these ranges that resins which can be cooked with the less unsaturated oils such as soybean oil and safflower oil to yield satisfactory varnishes are obtained. This matter of critical acid number is more fully discussed in connection with Fig. 2 hereinbelow.

The ester resins of this invention also have unusually high hydroxyl values. In the making of the resins an amount of pentaerythritol is employed which is substantially the chemical equiv-

alent of all of the acid ingredients employed. Hence, the esters contain pentaerythritol in reacted form in an amount which is substantially the chemical equivalent of all of the acid constituents of the esters. Since esterification is stopped at a very high acid value (as compared with the prior art practice in the making of ester-type resins), the esters will necessarily have unusually high hydroxyl values. The hydroxyl values of the esters may be determined by a special analytical procedure described infra and it has been found that the hydroxyl values of the resins of the invention fall within the range of from about 3.5 to about 7.6.

As above-stated, these resins are only partially esterified and contain a high degree of residual oil reactivity due to the presence of free hydroxyl and carboxyl groups. These esterifiable groups effect ester-interchange reactions with the soft oils in the varnish-making process. As a result of these ester-interchange reactions, mixed esters are formed. The ultimate result is that completely compatible oil-resin systems result at low acid values. The ester-interchange reactions referred to have other advantageous results. For example, the dried varnish films resemble alkyd resin films with respect to durability, flexibility, and general appearance.

The advantageous effect of the ester-interchange reactions of my resin and the soft oils will be lost if certain precautions are not exercised in the cooking of the varnish. The resins of this invention would gel if in the preparation thereof they were taken to low acid numbers, say below 50. Hence, it is desirable to avoid conditions in the cooking of varnishes that cause a lowering of the acid number of the resin without permitting any ester-interchange to take place. If the resin and oil are cooked together in proportions to form a 15-gallon or shorter varnish, and held on the upheal at 240° to 315° C. until clear, ester-interchange will take place and all of the advantages described hereinabove will obtain. If the rate of upheal is too rapid, or the viscosity of the oil is too great, the resin will remain insoluble in the oil and will gel per se. Should a varnish longer than 15 gallons be desired, the additional oil can be added after the clear point is reached.

The resins of the invention are prepared by reacting the desired rosin acid material, as for example wood or gum rosin, with the α,β -unsaturated polycarboxylic acid at a temperature productive of adduct formation. This reaction is sometimes referred to as Diene Synthesis. Effective temperatures for commercial operation are 180° to 210° C., although other temperatures known in the art may be used. This reaction is quite fast and is generally substantially complete in 20 or 30 minutes. The pentaerythritol is then rapidly added to the adduct and the two heated at an esterification temperature. For the esterification step a temperature of 230° C. to 265° C., for example, is satisfactory. An esterification catalyst may or may not be employed, as desired. The resin is held within the esterification temperature range for such a period as is necessary to provide a resin having an acid number within the above-mentioned critical range. When esterification has proceeded to the desired extent, the resin is cooled below the esterification temperature range and poured into containers.

Having now indicated in a general way the nature and purposes of the invention, there fol-

lows a more detailed description of specific embodiments of the invention. All parts and percentages in this specification and the claims appended hereto are by weight unless otherwise indicated.

EXAMPLE 1

A resin was prepared using the following raw material formulation:

	Parts
Rosin (N wood).....	1,000
Maleic anhydride.....	160
Pentaerythritol.....	250
Calcium acetate.....	3

The rosin employed contained about 90% rosin acids and 10% neutral bodies. Accordingly, there were present 2.98 mols of rosin acid. The molar ratio of maleic anhydride to rosin acid was 0.55. The pentaerythritol employed was a technical grade material containing about 84% pentaerythritol monomer and having a hydroxyl content of about 46.0%. The combining weight of pentaerythritol was 37.

The rosin and maleic anhydride were charged into a reaction kettle and heated to 200° C. over a period of 45 minutes. The pentaerythritol and calcium acetate were added to the resulting adduct over a period of 15 minutes. As a result of this addition the temperature dropped to 182° C. The mixture was then heated to 260° C. over a period of 35 minutes. The temperature was held at 260° C. for 15 minutes. The esterification reaction was stopped at this point by sparging the resin with water. The final resin had the following constants:

Color, M4 (U. S. rosin scale)
Acid number, 129
Hydroxyl value, 5.85
Softening point, 123° C. (Hercules drop method)

EXAMPLE 1 (a)

The following example illustrates the preparation of a 15-gallon soybean oil varnish from the resin of Example 1 in a closed kettle. The following raw material formulation was employed:

	Parts
Soybean oil (nonbreak)	463
Resin of Example 1	420

The resin and oil were heated in a closed kettle equipped with stirrer and thermometer under a blanket of CO₂ to 300° to 305° C. over a period of 6 hours and held at that temperature for a further period of 2 hours. The batch was then cooled to 235° C. in 2 hours and then thinned to 50% nonvolatiles using mineral spirits. The final varnish had the following constants:

Color, 8 minus (1933 Gardner scale)
Viscosity, G (Gardner-Holdt scale)
Drying time:
Dust free, 3½ hours
Tack free, 5 to 6 hours
Acid number of nonvolatile portion, 9

EXAMPLE 1 (b)

The following example illustrates the preparation of a 15-gallon soybean oil varnish from the resin of Example 1 cooked in an open kettle. The following raw material formulation was employed:

	Parts
Soybean oil (nonbreak)	463
Resin of Example 1	420

The resin and oil were heated to 310° to 315° C. in an open kettle for 1 hour and held at that temperature for an additional hour. The batch was then cooled to 300° C. in 12 minutes and held at that temperature for 30 minutes. The batch was further cooled to 235° C. in 1 hour and 25 minutes and then thinned to 50% non-volatiles using mineral spirits. The final varnish had the following constants:

Color, 10 minus (1933 Gardner scale)

Viscosity, D (Gardner-Holdt scale)

Drying time:

Dust free, 3½ hours

Tack free, 5 to 6 hours

Acid number of nonvolatile portion, 14

EXAMPLE 2

A resin was prepared using the following raw material formulation:

	Parts
Rosin (N wood)	1000
Pentaerythritol	250
Maleic anhydride	160
Zinc oxide	.8
Lithium carbonate	.5

The same types of rosin and pentaerythritol were employed as were employed in making the resin of Example 1. Also the same procedure for reacting the ingredients was employed, the zinc oxide and lithium carbonate being added to the adduct at the same time that the pentaerythritol was added thereto. The ultimate resin had the following constants:

Color, M (U. S. rosin scale)

Acid number, 130

Softening point, 125° C. (Hercules drop method)

This resin can be cooked with unbodied soybean oil to provide desirable varnishes. The same cooking cycles as shown in Examples 1 (a) and 1 (b) are required. The varnishes obtained are quite light in color.

EXAMPLE 3

A resin was prepared using the following raw material formulation:

	Parts
Rosin (N wood)	1000
Maleic anhydride	160
Pentaerythritol	250
Cadmium acetate.2H ₂ O	6.6

The same types of rosin and pentaerythritol were employed as were employed in Example 1. The procedure used in this example was the same as that of Example 1. A resin having the following constants resulted.

Color, N (U. S. rosin scale)

Acid number, 100

Softening point, 118° C. (Hercules drop method)

This resin can be cooked with soybean oil to provide very satisfactory varnishes. The cooking cycles required are substantially the same as those shown in Examples 1 (a) and 1 (b) hereof. The varnishes obtained are very light in color.

EXAMPLES 4-11, INCLUSIVE

A series of resins was prepared using varying ratios of maleic anhydride to rosin, starting with 10.0% and ending with 25%. The same types of rosin and pentaerythritol were employed as were employed in Example 1. One thousand parts of rosin were used in making each resin. The

pentaerythritol employed was held constant at 130 parts plus the additional amount required by the maleic anhydride. The catalyst employed was a zinc oxide-lithium carbonate catalyst, and it was employed in the amount of 0.8% zinc oxide and 0.5% lithium carbonate based on the rosin. Additional facts relative to composition of the resins appear in the following Table I.

Table I

Resin Designation	Resin Composition			
	Rosin Type	PE Parts	Per Cent Maleic Anhydride	Catalyst
Example 4.....	N wood...	130+188	25.0	ZnO—Li ₂ CO ₃ .
Example 5.....	do.....	130+131	17.5	Do.
Example 6.....	do.....	130+127.5	17	Do.
Example 7.....	do.....	130+120	16	Do.
Example 8.....	do.....	130+113	15	Do.
Example 9.....	do.....	130+101	13.5	Do.
Example 10.....	do.....	130+94	12.5	Do.
Example 11.....	do.....	130+75	10.0	Do.

The procedure of Example 1 was employed in making the resins. Zinc oxide-lithium carbonate catalyst was employed instead of calcium acetate. Esterification was stopped in each instance, with the exception of Example 4, such that a resin having an acid number of 138±10 resulted. In the case of Example 4, the esterification was stopped at an acid number of 190-200. The resins all had hydroxyl values of 5.6 to 6.4.

This series of resins was cooked into varnishes using the closed kettle method of Example 1 (a). In these cooks an unbodied alkali-refined soybean oil was used in an amount to make a varnish of 15 gallons length. During this process samples were removed at frequent intervals, diluted to 50% solids in mineral spirits and the solutions checked for viscosity. Gardner-Holdt viscosity tubes were employed. In the case of each cook, the viscosities obtained were plotted against the bodying time at 300° C. in minutes, using a logarithmic scale for the former and an ordinary scale for the latter. The bodying rate curves for all the varnishes are shown in Figure 1 of the attached drawing.

By proceeding as above-indicated, the bodying time to reach a viscosity of D was determined in each case. Hence, the following comparison obtains:

Table II

Varnish Designation	Bodying Time to Reach D Viscosity
	Minutes
Example 4.....	65
Example 5.....	104
Example 6.....	124
Example 7.....	140
Example 8.....	161
Example 9.....	190
Example 10.....	269
Example 11.....	283

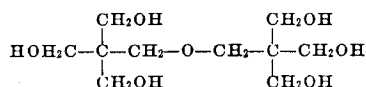
An inspection of the curves of Figure 1 and of the data in Table II indicates a difference in bodying characteristics of the high and low maleic-containing resins. There is a considerable difference between the 12.5% (Example 10) and 13.5% (Example 9) maleic resins with respect to the time required to achieve a D viscosity. In fact, in view of the data, 13.5% maleic anhydride based on the rosin marks a critical point at and above which there are obtained resins

which have unusually fast bodying action on soybean oil. It is significant to note that just above 13.5% maleic anhydride, probably at about 14.0%, the curves which represent the bodying rates of the resins change in form from true curves to straight lines. The practical upper limit for maleic modification appears to be about 25% maleic anhydride based on the rosin.

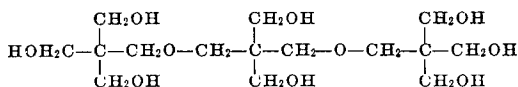
As the maleic or other α,β -unsaturated polycarboxylic acid concentration of these resins increases, their solubility in oil decreases. Resins with high α,β -unsaturated polycarboxylic acid concentrations are very reactive within themselves because of the high concentrations of free hydroxyl and carboxyl groups, and hence, tend to become insoluble when heated in oil before a part or all of the ester-interchange reactions have been effected. This, therefore, accounts for the maximum limit of about 0.86 molar ratio of α,β -unsaturated polycarboxylic acid to rosin acid.

The pentaerythritol employed in the foregoing examples was a commercial pentaerythritol which was a mixture of pentaerythritol monomer and polypentaerythritol. Specifically, it contained about 84% pentaerythritol monomer, the remainder being polypentaerythritols.

Pentaerythritol is made commercially by the condensation of acetaldehyde and formaldehyde. Along with the pentaerythritol monomer formed, there are formed comparatively small amounts of related hydroxylated substances. One of these compounds, dipentaerythritol, is an ether having the following structure:



Another related compound, tripentaerythritol, is formed in even smaller amounts. According to the best evidence, it is believed to have the following structural formula:



Dipentaerythritol, tripentaerythritol and higher ethers of pentaerythritol may be grouped together under the generic term "polypentaerythritols." This term is employed herein to mean those compounds having higher molecular weights than pentaerythritol monomer which are formed actually or theoretically by etherifying one or more of the hydroxyl groups of pentaerythritol monomer with other pentaerythritol molecules. The monomer, dimer, trimer, etc. of pentaerythritol refer to simple pentaerythritol, dipentaerythritol and tripentaerythritol, respectively. The term "pentaerythritol" is used herein in a generic sense to include both pentaerythritol monomer and pentaerythritol monomer-polypentaerythritol mixtures.

In accordance with this invention, the pentaerythritol employed in making the desired resins may be either substantially pure pentaerythritol monomer or pentaerythritol monomer-polypentaerythritol mixtures which contain at least 20% of pentaerythritol monomer and which have a hydroxyl content of at least 38%. Preferably, the pentaerythritol employed will contain at least 84% pentaerythritol monomer and will have a hydroxyl content of at least 46%.

Any rosin acid material may be used in preparing the subject resinous esters. By the term "rosin acid material" there is meant not only the substantially pure rosin acids but also commercial

wood and gum rosins, from which the substantially pure rosin acids are obtainable. Both wood and gum rosin contain neutral bodies, there being usually a somewhat lesser amount of neutral bodies in the latter than in the former. The term "rosin acid material" as used herein accordingly comprises wood and gum rosin, substantially pure rosin acids obtainable therefrom as by distillation, crystallization, etc., and specific rosin acids obtainable from such substantially pure rosin acids as abietic, 1-pimaric, d-pimaric, sapinic, etc., acids. The term also includes any of the aforesaid rosin acid materials which have been subjected to further treatment such as hydrogenation, dehydrogenation, disproportionation or heat-treatment. In the case of hydrogenation, it is preferred that the rosin acid material used as the starting material be hydrogenated to an extent that not more than 50% of the double bonds of the rosin acid contained therein is saturated with hydrogen. Tall oil rosin acid is another type of rosin acid material which may be used in carrying out this invention. Of these various materials, wood or gum rosin is preferred since its use is economically advantageous, and for the purpose of this invention it is as effective as the others.

Any α,β -unsaturated dicarboxylic acid such as maleic acid, fumaric acid, itaconic acid, citraconic acid, etc., may be employed in carrying out this invention. Similarly, the anhydrides of these acids may be employed and are to be regarded as true equivalents. Acids having 8 carbon atoms or less are preferred. Particularly preferred are maleic acid and maleic anhydride since they are available commercially and produce very desirable resins when used in accordance with this invention.

As stated in connection with the broad statement of the invention and as evidenced by Examples 4-11, inclusive, the proportion of α,β -unsaturated polycarboxylic acid to rosin acid is a critical factor in this invention. Examples 4-11, inclusive, show that the effective and critical range of maleic anhydride based on the rosin is from about 13.5% to about 25.0% by weight. Since the rosin employed in these examples contained 90% rosin acids, the critical range based on rosin acids is from about 15.0% to about 27.8%. When this range is converted to a molar basis, it is found that the critical range is from 0.46 to 0.86 mol of maleic anhydride per mol of rosin acid. This same critical range applies to α,β -unsaturated polycarboxylic acids and anhydrides generally.

The preferred molar ratio of α,β -unsaturated polycarboxylic acid to rosin acid is about 0.55. In a resin made from a rosin containing 90% rosin acid and maleic anhydride, this molar ratio corresponds with about 16% by weight of maleic anhydride based on the rosin.

As has been stated hereinbefore, the resins of this invention are partial esters having very high acid numbers are compared with prior art resins prepared from these same ingredients. Acid number is a critical property or factor to be taken into account in the preparation of the resins. For any particular molar ratio of maleic acid to rosin acid, there is a minimum acid number below which inoperable resins result in the sense that they generally remain insoluble and ultimately gel when it is attempted to cook them into a varnish with the less unsaturated soft oils such as soybean and safflower oils. This lower limit rises as the molar ratio of maleic acid to

rosin acid increases. The relationship which obtains can be seen by inspecting Figure 2. A series of resins were prepared by the procedures described herein from pentaerythritol, rosin, and maleic anhydride, using weight ratios of maleic anhydride to rosin from 13.5 to 25.0. (The corresponding molar ratios of maleic anhydride to rosin acid are 0.46 and 0.86, respectively.) The minimum acid numbers at which the resins could be successfully cooked into 15-gallon soybean oil varnishes without gelation of the resin were plotted against the molar ratios of maleic anhydride to rosin acid. Line AB of Figure 2 resulted. Substantially the same results are obtained regardless of the oil length used in the varnish preparation. Furthermore, other α,β -unsaturated polycarboxylic acids give substantially the same results as does maleic.

With respect to maximum acid number, it is only required that the esterification be carried far enough to give a homogeneous product. A homogeneous product is obtained when a resin of substantial clarity has been produced. As in the case of minimum acid number, the maximum acid number at which useful resins are produced varies with the molar ratio of α,β -unsaturated polycarboxylic acid to rosin acid and as this ratio increases a higher maximum obtains. Line CD of Figure 2 appears to represent this maximum acid number limitation for molar ratios from 0.46 to 0.75, although the line of demarcation between the operable and inoperable resins is not nearly so sharp here as in the case of the minimum limitation. Above the molar ratio of 0.75 there are maximum acid number limitations. The points, however, do not appear to fall on a smooth curve as in the case of molar ratios from 0.46 to 0.75.

As has also been stated previously, the resins of this invention have rather high hydroxyl values. In the making of the resins an amount of pentaerythritol is employed which is substantially the chemical equivalent of all of the acid ingredients employed. Some latitude is permitted in this respect, however, and amounts of pentaerythritol from the true chemical equivalent amount up to about 15% in excess thereof may be employed successfully in the preparation of the resins. It will be understood therefore that the phrase "substantially the chemical equivalent" is not to be limited to the actual chemical equivalent but is to be somewhat more broadly construed as above indicated. The resins of the invention have hydroxyl values within the range of from about 3.5 to about 7.6.

The procedure employed in forming the adduct of a rosin acid and an α,β -unsaturated polycarboxylic acid has been broadly described previously and has been specifically illustrated in the examples. The reaction is old and the temperatures which are effective are known to the art. These same statements apply to the esterification reaction. Since, however, the acid number of the resin is critical, the esterification reaction must be controlled so that the ultimate resin is within the critical range of acid number. Various techniques may be employed effectively for controlling the esterification reaction. However, water-sparging of the hot resin is particularly effective in that it stops the esterification reaction quickly and affords a very effective means for controlling the acid number of the resin.

An esterification catalyst may be employed if desired although it is by no means a necessary ingredient of the resin formula. A variety of in-

organic compounds can be used as catalysts. Generally, they are compounds which show an alkaline reaction in water, namely, those of the metals in groups I and II of the periodic table. In addition, litharge and lead acetate are also effective. These compounds are thought to promote ester-interchange reactions, as well as catalyze esterification reactions. They are used in amounts up to .3% based upon the rosin acid. Calcium and cadmium compounds are generally preferred since the final resins show a better color and maintain color stability in the soybean oil varnishes.

The soybean oil varnishes produced with the resins of this invention possess many desirable properties and consequently they are very useful both industrially and in the home. Such varnishes are light in color, dry quite fast, and produce films which are very hard and glossy. The drying time of the varnishes is of course a function of the oil length. In particular the 15-gallon soybean oil varnishes of the subject resins dry dust-free in about 3½ hours and tack-free in about 5 to 6 hours. In 24 hours the films are very hard and glossy. The general appearance of these films and their durability indicate that they resemble alkyd resin films (of the phthalic anhydride type) more closely than they do oleoresinous finishes. These varnishes can be used per se as vehicles for enamels or as blending agents with alkyd resins.

While the resins of this invention possess unique utility as a resin for use with soybean oil, they need not be used exclusively with that oil. In fact, they may be cooked with any drying oil, either alone or in admixture with soybean oil, to provide highly useful varnishes. Generally speaking, however, the resins are more adapted for use with the "soft drying oils" than they are with the "hard drying oils."

The oil length in which the resins of this invention can be used with any of the soft oils to form oleoresinous finishes varies over wide limits, viz., from 5- to 60-gallon lengths. However, with each oil a certain length yields a varnish with optimum properties. The optimum varnish oil length increases directly as the oil unsaturation increases. Optimum results obtain at 15-gallon length for soybean and safflower oils, 20-gallon length for linseed and dehydrated castor oils, and 23-25-gallon lengths for fish oils.

The resins of this invention are hard and crystal clear. The outstanding property of the resins is their ability to body the less unsaturated "soft" drying oils such as soybean and safflower oil at a fast rate—a rate sufficiently fast that the cooking cycles required to make varnishes of acceptable viscosity are of about the same length as those which obtain in the case of the prior art varnishes prepared from maleated rosin esters and linseed or dehydrated castor oils. In view of the short cooking cycles, the varnishes produced are light in color. Furthermore, in other respects these soybean oil varnishes are quite similar to the prior art linseed oil and dehydrated castor oil varnishes. Hence, by means of the resins of this invention it has become possible to overcome the major defects of soybean oil and safflower oil as varnish oils, i.e., the long cooking cycles and the resultant extremely poor color of the varnishes.

The special analytical procedure referred to supra for the determination of hydroxyl value is that given in "Commercial Methods of Analysis," F. D. Snell and F. M. Biffen, McGraw-Hill Book Co., Inc., 1st Ed., page 439, except for the

modification described below. The resins of this invention, when acetylated in accordance with the reference, generally form insoluble products on titration with NaOH solution. For this reason, the procedure of the reference is modified as follows. When ready to titrate, add phenolphthalein indicator to the acetylated resin solution and titrate nearly to the neutral point. Separate the soluble and insoluble fractions of the resulting mixture either by decantation or filtration. Dissolve the residue with 75 ml. of neutral 2:1 benzene-alcohol solution, using heat if necessary. Titrate both the filtrate and the solution of the residue, after cooling it, with about 0.25 N alcoholic KOH solution, using about 10 drops of 1% phenolphthalein indicator solution. Record the volume of alcoholic KOH required. By proceeding in this manner all of the excess acetic acid and any of the titratable acidity of the resin will be titrated. In calculating the hydroxyl value a correction must of course be applied for any titratable acidity present in the resin.

What I claim and desire to protect by Letters Patent is:

1. A hard resin suitable for cooking with soybean and similar oils to provide an oleoresinous varnish which comprises a resinous ester of a pentaerythritol and an adduct of a rosin acid material and an aliphatic α,β -ethylenically unsaturated polycarboxylic acid, said ester containing from 0.46 to 0.86 mol of said α,β -unsaturated polycarboxylic acid in reacted form per mol of rosin acid, said ester containing a pentaerythritol in reacted form in an amount which is substantially the chemical equivalent of all of the acid constituents of the ester, said ester having an acid number which is low enough to provide an ester of substantial clarity but which at the same time is not below line AB of Figure 2.

2. A hard resin suitable for cooking with soybean and similar oils to provide an oleoresinous varnish which comprises a resinous ester of a pentaerythritol and an adduct of a rosin acid material and maleic acid, said ester containing from 0.46 to 0.86 mol of maleic acid in reacted form per mol of rosin acid, said ester containing a pentaerythritol in reacted form in an amount which is substantially the chemical equivalent of all of the acid constituents of the ester, said ester having an acid number which is low enough to provide an ester of substantial clarity but which at the same time is not below line AB of Figure 2.

3. A hard resin suitable for cooking with soybean and similar oils to provide an oleoresinous varnish which comprises a resinous ester of a pentaerythritol and an adduct of rosin and maleic acid, said ester containing from 0.46 to 0.86 mol of maleic acid in reacted form per mol of rosin acid, said ester containing a pentaerythritol in reacted form in an amount which is substantially the chemical equivalent of all of the acid constituents of the ester, said ester having an acid number which is low enough to provide an ester of substantial clarity but which at the same time is not below line AB of Figure 2.

4. A hard resin suitable for cooking with soybean and similar oils to provide an oleoresinous varnish which comprises a resinous ester of a pentaerythritol and an adduct of rosin and maleic acid, said ester containing about 0.55 mol of maleic acid in reacted form per mol of rosin acid, said ester containing a pentaerythritol in reacted form in an amount which is substantially the chemical equivalent of all of the acid constituents of the

ester, said ester having an acid number which is low enough to provide an ester of substantial clarity but which at the same time is not below line AB of Figure 2.

5. A hard resin suitable for cooking with soybean and similar oils to provide an oleoresinous varnish which comprises a resinous ester of a pentaerythritol and an adduct of rosin and maleic acid, said ester containing from 0.46 to 0.86 mol of maleic acid in reacted form per mol of rosin acid, said ester having a hydroxyl value of from 3.5 to 7.6, said ester having an acid number which is low enough to provide an ester of substantial clarity but which at the same time is not below line AB of Figure 2.

6. A hard resin suitable for cooking with soybean and similar oils to provide an oleoresinous varnish which comprises a resinous ester of a pentaerythritol and an adduct of a rosin acid material and maleic acid, said ester containing from 0.46 to 0.86 mol of maleic acid in reacted form per mol of rosin acid, said ester containing a pentaerythritol in reacted form in an amount which is substantially the chemical equivalent of all of the acid constituents of the ester, said pentaerythritol being selected from the group of pentaerythritol monomer and pentaerythritol monomer-polypentaerythritol mixtures which contain at least 20% of pentaerythritol monomer and which have a hydroxyl value of at least 38%, said ester having an acid number which is low enough to provide an ester of substantial clarity but which at the same time is not below line AB of Figure 2.

7. A hard resin suitable for cooking with soybean and similar oils to provide an oleoresinous varnish which comprises a resinous ester of pentaerythritol monomer and an adduct of a rosin acid material and maleic acid, said ester containing from 0.46 to 0.86 mol of maleic acid in reacted form per mol of rosin acid, said ester containing pentaerythritol monomer in reacted form in an amount which is substantially the chemical equivalent of all of the acid constituents of the ester, said ester having an acid number which is low enough to provide an ester of substantial clarity but which at the same time is not below line AB of Figure 2.

8. A hard resin suitable for cooking with soybean and similar oils to provide an oleoresinous varnish which comprises a resinous ester of a pentaerythritol and an adduct of a rosin acid material and maleic acid, said ester containing from 0.46 to 0.86 mol of maleic acid in reacted form per mol of rosin acid, said pentaerythritol being selected from the group of pentaerythritol monomer and pentaerythritol monomer-polypentaerythritol mixtures which contain at least 20% of pentaerythritol monomer and which have a hydroxyl value of at least 38%, said ester having a hydroxyl value of from 3.5 to 7.6, said ester having an acid number which is low enough to provide an ester of substantial clarity but which at the same time is not below line AB of Figure 2.

9. A hard resin suitable for cooking with soybean and similar oils to provide an oleoresinous varnish which comprises a resinous ester of a pentaerythritol and an adduct of a rosin acid material and maleic acid, said ester containing from 0.46 to 0.86 mol of maleic acid in reacted form per mol of rosin acid, said ester containing a pentaerythritol in reacted form in an amount which is substantially the chemical equivalent of all of the acid constituents of the ester, said pentaerythritol being a pentaerythritol monomer-

polypentaerythritol mixture containing at least 84% of pentaerythritol monomer and having a hydroxyl value of at least 46%, said ester having an acid number which is low enough to provide an ester of substantial clarity but which at the same time is not below line AB of Figure 2.

10. A hard resin suitable for cooking with soybean and similar oils to provide an oleoresinous varnish which comprises a resinous ester of pentaerythritol monomer and an adduct of rosin and maleic acid, said ester containing from 0.46 to 0.86 mol of maleic acid in reacted form per mol of rosin acid, said ester containing a pentaerythritol in reacted form in an amount which is substantially the chemical equivalent of all of the acid constituents of the ester, said ester having an acid number which is low enough to provide an ester of substantial clarity but which at the same time is not below line AB of Figure 2.

11. A hard resin suitable for cooking with soybean and similar oils to provide an oleoresinous varnish which comprises a resinous ester of a pentaerythritol and an adduct of rosin and maleic acid, said ester containing from 0.46 to 0.86 mol of maleic acid in reacted form per mol of rosin acid, said ester containing a pentaerythritol in reacted form in an amount which is substantially the chemical equivalent of all of the acid constituents of the ester, said pentaerythritol being a pentaerythritol monomer-polypentaerythritol mixture containing at least 84% of pentaerythritol monomer and having a hydroxyl value of at least 46%, said ester having an acid number which is low enough to provide an ester of substantial clarity but which at the same time is not below line AB of Figure 2.

12. A hard resin suitable for cooking with soybean and similar oils to provide an oleoresinous varnish which comprises a resinous ester of a pentaerythritol and an adduct of a rosin acid material and an α,β -unsaturated polycarboxylic acid, said ester containing from 0.46 to 0.86 mol of α,β -unsaturated polycarboxylic acid in reacted form per mol of rosin acid, said ester having a hydroxyl value of 3.5 to 7.6, said ester having an acid number which is low enough to provide an

ester of substantial clarity but which at the same time is not below line AB of Figure 2.

13. A hard resin suitable for cooking with soybean and similar oils to provide an oleoresinous varnish which comprises a resinous ester of a pentaerythritol and an adduct of a rosin acid material and maleic acid, said ester containing from 0.46 to 0.86 mol of maleic acid in reacted form per mol of rosin acid, said ester containing a pentaerythritol in reacted form in an amount between that which is the chemical equivalent of all of the acid constituents of the ester to a 15% excess thereof, said ester having an acid number which is low enough to provide an ester of substantial clarity but which at the same time is not below line AB of Figure 2.

14. A hard resin suitable for cooking with soybean and similar oils to provide an oleoresinous varnish which comprises a resinous ester of a pentaerythritol and an adduct of a rosin acid material and maleic acid, said ester containing from 0.46 to 0.86 mol of maleic acid in reacted form per mol of rosin acid, said ester containing a pentaerythritol in reacted form in an amount which represents from 2% to 8% in excess of the chemical equivalent of the acid constituents of the ester, said ester having an acid number which is low enough to provide an ester of substantial clarity but which at the same time is not below line AB of Figure 2.

15. A hard resin suitable for cooking with soybean and similar oils to provide an oleoresinous varnish which comprises a resinous ester of a pentaerythritol and an adduct of rosin and maleic acid, said ester containing from 0.46 to 0.86 mol of maleic acid in reacted form per mol of rosin acid, said ester containing a pentaerythritol in reacted form in an amount which represents from 2% to 8% in excess of the chemical equivalent of the acid constituents of the ester, said ester having an acid number which is low enough to provide an ester of substantial clarity but which at the same time is not below line AB of Figure 2.

ALFRED E. RHEINECK.

No references cited.