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ESTER RESIN COMPOSITIONS

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This invention relates to coatings and compositions intended for coatings. A particularly difficult field for coatings, for example, is that of wire enamel for electrical insulation on account of the peculiar demands in that field. In addition to hardness, adhesion and resistance to the action of solvents, wire enamels to be satisfactory should have a high degree of flexibility and resistance to scrape and abrasion, should not soften or become brittle as the temperature is elevated or depressed and should not lose adhesion over the temperature range to which they may be subjected. The usual types of wire enamels made from drying oils and resins such as cumar, rosin, natural resin, etc., become brittle merely on aging, they have low abrasion and scrape resistance, and they readily soften or dissolve in toluol, acetone and the like.

The present invention provides compositions that are peculiarly well fitted for enameling wires in that they can be made by baking to yield very tough abrasion-resistant films of high flexibility and high resistance to toluene, acetone, etc. without softening when exposed to temperatures as high as 200° C. and retaining the original flexibility at temperatures of about 125° C. for an extended period without becoming brittle or losing adhesion. Moreover, the compositions as prepared for application are readily soluble in coal tar solvents or thinners; such solutions can be cold or hot blended with compositions made from drying oils and oil-soluble phenolic resins, and the resulting blends have improved resistance to solvents and abrasion.

Compositions in accordance with this invention and intended for baked wire enamels and other protective coatings depend upon ester resins obtained in the reaction of a cyclopentadiene adduct of maleic acid or its anhydride with a polyhydric alcohol as glycerol together with a monobasic acid derived from a drying or semi-drying oil. It has been found, moreover, that the usefulness of these compositions as coatings is in addition dependent upon the relative proportions of the reactants and that the practice developed in the manufacture of the typical alkyd resins, i. e. the glycerol phthalates, cannot be followed in this respect.

To meet the requirements of durability, flexibility, adhesion, etc. in films of the ester resin alone after baking or air drying and to retain these properties after aging over an extended period, a drying fatty or monobasic acid ingredient calculated as triglyceride should constitute at least 50 per cent of the reaction mass unless the product be further plasticized with an agent such as tricresyl phosphate, dibutyl phthalate, etc. or

a non-drying monobasic acid, such as derived from peanut or cotton seed oil, be substituted in whole or in part for the drying fatty acid or a fatty oil be incorporated in addition. The amount of drying fatty acid which can be included above 50 per cent for durable flexible hard films cannot be determined with definiteness; a composition for instance having 63 per cent by weight (molar proportion) of soya fatty acids polymerizes rapidly under heat and yields hard flexible films on either air-drying or baking, but it can be further extended with a drying oil and still give useful coatings. In these respects the ester resins of this invention differ markedly from the typical alkyd resins in which as a rule less than 50 per cent of drying fatty acid calculated as triglyceride can be incorporated for the production of hard baking finishes and then only with the acids of the harder drying oils.

The fatty acids in the above described reaction include fatty acid obtained from drying or semi-drying vegetable oils; they are normally commercial acids derived from oils and contain such components as oleic, linoleic, linolenic, etc. The acids can be substituted by their monoglycerides and also their triglycerides when the latter have been oxidized generally to an iodine value of about 105–135; modified or dehydrated non-drying oils or their fatty acids as dehydrated castor oil, and thereby made useful for coating compositions, are other possible substitutes. The maleic acid adducts can be replaced in part, and retain the desirable properties which the adducts impart, by oil-soluble phenolic resins as those prepared from alkyl or aryl substituted phenols, hydroxy phenols, etc. The polyhydric alcohols include glycol, glycerol, sorbitol, mannitol, pentaerythritol, etc., their homologs and polymers.

The ester resins in general have acid values ranging from about 10 to 90. They are heat reactive, and they can be used for baking operations without modification by the incorporation of other ingredients, particularly when the fatty acid reactant or its equivalent is 50 per cent or more of the total. For air-drying coating compositions, however, they are primarily useful as intermediates for incorporation in drying oils.

The complex ester resins of the present invention are readily soluble in drying and semi-drying fatty oils without the addition of rosin, ester gum or other solubilizing agent; and they are particularly useful in conjunction with oils that are normally slow drying. They appear unique among ester or alkyd resins in having a most marked accelerating effect on the drying

of oils and hardening effect thereon without separating out and particularly on semi-drying oils as cotton seed, corn, etc., or slow drying oils including linseed, soya bean, perilla, rapeseed, i. e. oils which do not possess conjugated double bonds. When included in a slow drying oil such as linseed, they form varnishes which can be processed on a time cycle comparable to those prepared from conjugated double bond oils as tung or oiticica oils, and the final acid value of the reaction product is comparable to or lower than the oil processed alone. These oil varnishes deposit films which polymerize rapidly upon contact with the air, i. e. air-dry within two or three hours to solid coatings of pale color and improved hardness and alkali resistance; and upon baking at temperatures as low as 95° C. the films solidify within a few minutes.

In preparing an oil composition incorporating an ester resin as herein defined the mass of oil and resin is preferably cooked or processed at a temperature of 175° C. or above, for at this temperature a reaction apparently takes place as evidenced by a change in the oil. For example, linseed oil of a viscosity Q (measured by a Gardner-Holdt viscosimeter) if cooked alone for 40 to 45 minutes at 250° C. shows very little change in viscosity; but if one part of the ester resin is added to four parts of the same linseed oil and the mass heated at 250° C., there is a rapid increase in the mass viscosity and within a period of 40 to 45 minutes the mass becomes completely solid. With oils having conjugated bonds, such as oiticica and tung oil, the reaction is extremely rapid; a 1:2 ester resin and tung oil composition polymerize at 250° C. in 5 to 8 minutes and a 1:4 ester resin and tung oil composition polymerize in 10 to 12 minutes, whereas tung oil alone requires about 24 minutes at this temperature. The viscosity increase is of the same order as the polymerization rate; and the long induction period, which may be several hours during which there is very little increase in viscosity when using with drying oils such resins as the glycerolphthalates, natural resins and modified phenolic resins, is practically eliminated. For many applications as in coating leather or textiles a highly polymerized product is desirable to overcome penetration.

The rate of viscosity increase and polymerization can be accelerated by first heat-treating the oil at 260° to 315° C. and thus raising its viscosity to a Z2 or Z4 value; when linseed oil of the increased viscosity is processed with the ester resin described, the rate of polymerization of the resulting composition is accelerated and is more rapid than that obtained with a corresponding composition formulated with a body Q linseed oil. The composition based on the higher bodied oils also yields a harder film on air-drying. Moreover, when the viscosity of the composition approaches the higher viscosity as indicated above, the composition shows great reactivity on the surface exposed to the air; in order to retain this reactivity, it is preferably carried to the desired viscosity under an inert atmosphere and the forming of insoluble surface products prior to reduction with thinner is avoided. There are definitely two reactions which take place in the composition, polymerization and surface reactivity, and these can be noted by physical tests and observation.

The ester resins can be included in oils in any proportions and the compositions can be modified with rosin, ester gum, oil-soluble phenolic resins,

alkyd resins, etc. Extremely long oil compositions, containing as much as 90 per cent of oil, are found to retain the properties of heat-reactivity and of polymerization; such compositions find utility as drying oil substitutes, and soya bean oil for example is so improved with 10 per cent of the ester resin as to approach tung oil by polymerizing or solidifying at about 250° C. within 50 minutes. At the other extreme of short oil compositions having only about 10 per cent of oil there is obtained compositions which when baked and particularly when plasticized yield hard, tough and highly resistant coatings; suitable plasticizers include the well known resin plasticizers as triphenyl phosphate, tricresyl phosphate, dibutyl phthalate, etc.

The oil and resin compositions, particularly when the resins are made with soya bean oil fatty acid or monoglyceride yield films of a very pale color and hardness, and the color is remarkably fast which permits their use for preparing white enamels showing little if any change in color on aging. They are also characterized by a marked improvement in gloss retention upon exposure to weathering as compared with a composition of linseed oil, for instance, made with a resin such as ester gum or a rosin-modified phenolic resin. The high gloss coupled with rapid hardening make them useful for printing inks when using perilla, linseed oil or the like, and adding the usual pigment as carbon black, Prussian blue, etc.

The soft liquid ester resins as herein described are also compatible with cellulose esters, such as nitrocellulose, ethyl cellulose, etc., to yield films which are flexible with excellent adhesion and the hardness of the films is greater than that of films obtained with hard resins, such as ester gum and cumar; these results are contrary to expectations, since soft liquid resins in general act as plasticizers to soften films, and the hardness is apparently due to the fact that the reactivity of the resins is not materially modified by the presence of the other ingredients. Likewise, the ester resins blend with other alkyd resins whereby the latter are made more heat-reactive in correspondence with relative proportions.

Ester resins

The ester resins of the present invention obtained by the reaction of glycerol or other polyhydric alcohol with a cyclopentadiene adduct of maleic acid and a monobasic acid are, in general, made by charging into a kettle the alcohol and the adduct and raising to a temperature approximating 190 to 200° C. at which the charge is held for a few minutes; the fatty acid or equivalent is then added to the charge, preferably in portions and bringing the batch up to temperature after each addition, and the mass is cooked at this temperature until the desired acid value and polymerization is obtained. The order in which the reactants are charged into the kettle, however, can be altered without affecting the product. The temperatures at which the batches are run depend upon the ingredients and proportions but are normally in the neighborhood of 190 to 200° C. when atmospheric pressure is used. As before indicated, about 0.65 mol of fatty acid per mol or more of the adduct is normally required, and enough polyhydric alcohol is added to give the degree of esterification required and the final low acid end products on further processing. For solution in oils ester

resin products in the liquid form are generally desired as the intermediates, and the intended use of the compositions as coatings becomes another limiting factor determining the relative proportions of the reactants.

Example 1.—About 750 parts of the cyclopentadiene adduct of maleic anhydride and 354 parts of glycerine were reacted together for about 15 minutes at 200° C. Then a mixture of 300 parts linseed fatty acids and 700 parts soya bean fatty acids were slowly added to the charge and the reaction continued for about 4 hours at 200° C.; the fatty acids constituted about 55 per cent of the product. A very pale liquid resin with an acid value of about 35 to 50 was obtained, and one readily soluble in linseed or tung oil. On continued heating at 200° C. the final end point was a rubbery infusible gel.

Example 2.—About equal parts of the maleic anhydride adduct and blown linseed oil with an iodine value of about 105–135 and about twenty per cent of glycerine based on the weight of resin and oil were reacted in accordance with the procedure of the foregoing example. The resulting liquid resin was a clear intermediate that could be reacted with linseed and other oils to form coating compositions; upon further heating the liquid resin was converted to a solid rubbery gel that could be calendered on a flexible base. A similar product was obtained when blown soya bean oil was substituted.

Example 3.—420 parts of the adduct of maleic anhydride and 219 parts of glycerine were raised to 210° C. in twenty minutes and held for a few minutes. Linseed fatty acid in three portions of 187 parts each were added one at a time, regaining the temperature after each addition. After heating for 2½ hours about 20 parts of glycerine were added and the reaction continued until the acid number was reduced to 47. The fatty acid reactant constituted about 55 per cent of the resin which was very hard but remained flexible; it could therefore be used alone for coatings. One part of this liquid resin added to two parts of tung oil caused polymerization at 250° C. in 5 minutes, whereas the same tung oil heated alone at 250° C. required four times as long a period.

To demonstrate the differences in properties between the maleic anhydride adduct resin and one obtained with phthalic anhydride, a resin was made of the same formulation as above but substituting phthalic anhydride. Solutions at equivalent viscosities of these resins were flowed on glass plates and baked, and the hardness of the films was measured (Gardner-Holdt swinging beam); films of the phthalate resin with a 15 minute bake had a hardness of 28–30 seconds and at the end of an hour one of 78–91 seconds as compared with 66 seconds at 15 minutes and 220–228 seconds at the end of an hour characterizing the resin of this example. Substituting the soya bean and linseed oil fatty acid mixture of Example 1 in the above formula did not reduce appreciably the hardness of film obtained.

Example 4.—About 100 parts of the maleic anhydride adduct and 44 parts of the glycerine were heated up to about 190° C. and held for a few minutes. To this was added 30 parts of linseed fatty acid and 70 parts of soya bean fatty acid divided into three equal portions and the temperature raised to about 190° to 200° C. after each addition. When held at this temperature for about 2 hours a soft viscous resin intermediate of pale straw color and having an acid value

of 35 to 50 was obtained. The resin readily dispersed in linseed oil or China-wood oil, and on further heating polymerized to a solid state more rapidly than the oils alone. The resin heated alone at 250° C. polymerized to a solid gel state in 9 to 10 minutes at 250° C., whereas on reduction with China-wood oil in the proportion of one part of resin to two of oil, the polymerization time to the solid gel state is 5 minutes at 250° C. and of the China-wood oil alone it is about 22 minutes at 250° C.

Example 5.—1200 parts of the maleic anhydride adduct and 620 parts of pentaerythritol were run to 200° C. and held for 5 minutes. Then 1200 parts of soya bean fatty acids were added and the reaction continued at 200° C. for about one and one-half hours. The resin was reduced with xylol and drier added. The resulting composition air-dried as a film to a surface of extreme hardness. When baked as a film on paper at 135° C. the coating was flexible and hard and showed no softening on immersion for 12 days in toluol, acetone or alcohol; this indicates its usefulness as interliners for bottle caps.

The resin of this example yields an extremely hard coating. It is particularly useful as a blending base and hardener for soft phthalic alkyds and varnishes, and as a constituent in cellulose lacquers. It can also be plasticized by the addition of a low percentage of drying oil. As a clear coating it yields a hard flexible film when applied as a very thin film. When pigments are incorporated and applied in the film thickness of a normal coating composition, the resulting film may crack on bending; but the ester resin can be plasticized with soft alkyds, oils or plasticizers for use in pigmented coatings that retain flexibility and yield high film hardness.

The ester resin of this example was modified by increasing the fatty acids to 2400 parts and then it was reduced to a viscosity D with xylol and a trace of cobalt and manganese drier added; a white enamel was made by adding titanium oxide and zinc oxide and thinned with Varsol to spraying consistency. The enamel set dust free in 1 to 1½ hours and became hard on air-drying in 3 to 4 hours; on further drying it became extremely hard sufficient for wet sanding and polishing, and yet it retained flexibility so as to withstand sharp bending without cracking.

The ester resin of this example was mixed with nitrocellulose in the ratio of 50 parts to 100 parts of nitrocellulose, and 50 parts of xylol were added. The lacquer hardened rapidly to a hard flexible coating with good resistance to water, greases and solvents.

Other polyhydric alcohols which were tried in equivalent proportions as substitutes for glycerol included glycol, sorbitol and mannitol; useful products were obtained in each case.

Example 6.—The adduct of maleic anhydride can be substituted in part by oil-soluble phenolic resins to yield products having a heat-reactivity that includes an accelerating action on the gelation of oils. For instance 90 parts of a resin, made from about equal parts of paraphenyl phenol and formaldehyde, and about 10 parts of the adduct were reacted with 6 parts of glycerine for about 4 hours at about 200° C. The resin was hard, reactive and oil-soluble. The proportions of phenolic resin to adduct can be varied as desired.

Example 7.—As an illustration of a partial substitution by an oil-soluble hydroxy-acid resin, a resin of that type was prepared from 100 parts of para-hydroxybenzoic acid, 100 parts of formal-

dehyde. (37 per cent aqueous solution of formaldehyde) in the presence of 2 parts of oxalic acid; the product was thereupon reacted with 200 parts of abietic acid and 24 parts of glycerine. Of this resin 20 parts were mixed with 80 parts of the adduct of maleic anhydride and 44 parts of glycerine and the batch was run to 190° C. over a period of about one-half hour. Then there were added 70 parts of linseed fatty acids and 30 parts of soya bean fatty acids in aliquot portions and held at about 200° C. for 2 to 3 hours or until a soft viscous resin of pale straw color was obtained with an acid value of 25 to 50. The ester resin obtained readily cold blended with drying oils.

A resin of similar type was prepared but substituting about 10 per cent of polyvinyl alcohol for an equivalent amount of glycerine giving a resin with an acid value of about 80 to 110.

Example 8.—A liquid oil-soluble and heat-reactive resin was made from a monoglyceride of linseed oil prepared by reacting glycerine with linseed oil in the presence of litharge; for instance, a mono-glyceride can be made by heating the linseed oil with about two molar proportions of glycerol in the presence of about one-half of one per cent of litharge and held at a temperature of about 210°–230° C. until homogeneous. To 209 parts of the monoglyceride were added about 8 parts of glycerine and 123 parts of the maleic anhydride adduct. The mass was reacted about 4 hours at about 200° C. or until the acid value was about 40 to 45. During the reaction the mass was blanketed with CO₂. The resin applied as a thin film hardened very rapidly on baking at 100° C. to a flexible extremely hard coating of pale color and resistance to solvents, water and greases and durable on exposure to weather. It was very reactive with drying oils such as linseed, dehydrated castor and perilla oil, especially when the oils were bodied to viscosity of Q to Z2. The rapid rate of polymerization when added to tung oil and the film heated at 250° C. is shown by a polymerization time of a composition of one part of resin to two of oil of about 8 minutes and of a one to four composition of about 14 minutes.

Coating compositions

Ester resins, as described in the above Example 1 for instance, form useful coating compositions by reducing them to the right consistency with volatile solvents such as hydrocarbon thinners, coal tar solvents and the like; in this form they are particularly useful as wire enamels. For enameling wire the coatings are customarily applied in four or five successive layers and baked to temperatures of about 200° C. and preferably 300° C. or above, and it is highly desirable that these layers be applied at very short time intervals. The coatings here described can be applied at intervals of less than 60 seconds to yield upon baking at the temperatures stated tough, abrasion-resistant films of high flexibility and high resistance to solvents. They show no softening upon exposure to temperatures of 200° C. and retain their original flexibility when heated at 125° C. for an extended period and without loss of adhesion. The solutions in volatile solvents, however, find utility for applications other than wire enamels, and on the other hand drying oil compositions can be employed in the preparation of wire enamels or coatings.

Example 9.—For a coating composition made from the resin of Example 4, the resin was reduced to a viscosity D with xylol and cobalt drier equivalent to .018 per cent cobalt on solids was

added. The coating air dried to a hard film in 2½ to 3½ hours with an initial set time of 1 to 1½ hours. The same composition applied to paper and baked for 30 minutes at 125° C. gave a hard flexible film without softening on immersion in toluol, alcohol or acetone. The composition, when baked as a thin film on tin for 10 to 20 minutes at 175° to 200° C., was extremely hard but flexible enough so that caps could be stamped out of flat coated stock without any fracture on the bend or loss in adhesion on immersion in boiling water for 5 minutes. It is therefore well suited as linings for cans as well as enameling for wire and other uses.

The solution of ester resin in volatile solvents can be blended with other varnishes as for instance one made from an oil-soluble resin and a drying oil. This is illustrated by the following example:

Example 10. An ester resin made in accordance with Example 4, but substituting 133 parts of linseed fatty acids in place of 30 parts of linseed fatty acids and 70 parts soya bean fatty acids, was reduced with a coal tar solvent. This was cold blended in equal parts with a varnish consisting of 100 parts of an oil-soluble resin made from para-phenyl-phenol and 200 parts of tung oil which had been run to 200° C., held for 2 to 3 hours, and reduced with solvent to 50 per cent solids. The product is well suited as a wire enamel.

The coating compositions prepared by means of volatile solvents can also be applied as protective coverings over other varnish coatings without injury to or lifting of the underneath coatings.

Example 11.—A wire enamel having high resistance to solvents and suitable as a solvent resistant top coat over a phenolic resin oil varnish base, was made by reacting together

	Parts
Maleic acid adduct of cyclopentadiene.....	100
China-wood oil fatty acids.....	200
Pentaerythritol	75

at a temperature of 200° C. for a period of 30 to 45 minutes and then reduced with solvent to a solid content of 50 per cent solids. When applied and baked on a wire enameling machine at a temperature above 500° F. it yielded a flexible hard film with high resistance to solvents. There was no deleterious effect on the primer or under coat.

Resin-oil compositions

The ester resins of the above examples in their liquid or viscous form can be incorporated in various ways with oils, bodied or unbodied, to yield air-drying or baking coating compositions. The oils include drying and semi-drying oils and in addition modified or dehydrated non-drying oils which are thereby made useful for coating compositions; these various types are herein designated as drying oils.

Example 12.—When the ester resin of Example 1 was mixed with linseed oil, in the proportion of one of resin to four of oil the varnish had a high body upon heating for 30 minutes at 450 to 500° F. and an acid value of from 2 to 8 (depending on the oil used). It yielded a solid film on baking for 7 minutes at 95° C. which was very pale in color. Because of the high degree of reactivity with drying oils the ester resin is particularly useful for treating slow drying oils; and the varnishes can be reduced with ester gum or cheapening ingredients and still yield finishes

competing in cost and speed of drying with varnishes made from fast drying oils.

Example 13.—The resin of Example 1 when extended with about 10 per cent of linseed oil of body Q reacted rapidly on heating to 240° C. to a dry pulverizable mass. Such products find particular utility as binders for brake linings.

Example 14.—Diluents such as ester gum have only a slight retardation factor on polymerization of the resins. About 40 parts of the resin of Example 1 were mixed with 40 parts of ester gum and about 37 pounds of bodied perilla oil Z2 (Gardner-Holdt viscosimeter). The mass was raised to a temperature of about 250° C. within a half hour and held for a few minutes and about 74 parts more of the oil were slowly added; the temperature of 250° C. was again reached and held for a few minutes. Then the reaction was checked by stirring in about 20 parts more of ester gum and the mass cooled and thinned with an equal weight of mineral spirits. The product had a viscosity of E (Gardner-Holdt scale) with a non-volatile of about 50 per cent and a color of 4-5 (as determined by a Hellige comparator). It dried fairly hard in about 1½ hours to give a film of high gloss and pale color.

Various other resins as cumar, Congo and rosin can be substituted for ester gum, and the proportions can be widely varied. These serve as diluents and thus to stabilize the reaction. Pigments can also be added for producing enamels.

Example 15.—One part of the resin of Example 3 was mixed with 1 part of linseed oil (body Q) and gradually heated. Upon reaching a temperature of about 260° C. the viscosity increased so rapidly that it was necessary to check with another part of the linseed oil, and again on reaching 260° C. the mass became viscous; it became a solid gel on heating to 275° C. The same ingredients in the same proportions were heated after the second addition of linseed oil to about 230° C. and reduced with Varsol to a viscosity E; the varnish had a solids content of 60 per cent. A trace of drier was included. In a baking test at 125° C. a film of the varnish set in one to three minutes to a dry surface and without any wrinkling; and when the baking was continued for 30 minutes the film had a hardness of 21 sec. (by the Gardner-Holdt swinging beam method).

Example 16.—The resin of Example 4 was run with an equal weight of linseed oil heat-bodied to viscosity N to 200° C. and then to about 260° C. when 3 more parts of the linseed oil were included. The mass was again run to 260° C., cooled and checked with mineral spirits to a solution having a solids content of 70 per cent; it had an acid number of 2.9 and a color of 3-4. The varnish in a thin film rapidly polymerized on baking at a temperature as low as 68° C. Such a composition has particular utility as a vehicle in printing inks, having a high gloss and flow and rapidly hardening on heating. On account of its neutral condition the composition can be pigmented with zinc oxide and other basic pigments.

Uses

The ester resins of this invention have found a wide variety of uses or applications. In addition to coatings on metals, etc. they form excellent saturants prior to polymerization for paper, felt, cloth, etc. since they wet and penetrate readily, and upon polymerization they greatly improve the toughness of the impregnated material; for this purpose they are usually thinned to 50 to 70 per cent solids. They likewise show adhesion to such surfaces as rock wool and glass fibers and form desirable binders for them. Instead of thinning with solvents they can be dispersed as emulsions or suspensions in water or other liquids and used in this form as saturants or binders; triethanolamine and other emulsifying agents can be included, and an almost clear emulsion is obtained with proportions of one part of the resin to 1 to 2 parts of water. From 70 to 90 per cent of the resin have been incorporated in casein paints and found to dry to impermeable waterproof films; from 30 to 60 per cent have been added to water-soluble urea resins to give coatings as on felt similarly characterized. They have also been incorporated as modifying agents for alkyd resins in amounts varying from 20 to 30 per cent of the alkyd resins for auto finishes and metal enamels with a greatly improved hardness.

What is claimed is:

1. Ester resin comprising the reaction product of a cyclopentadiene adduct of maleic anhydride with a polyhydric alcohol and a reactant selected from the group consisting of fatty acids of drying and semi-drying oils, their monoglycerides and their oxidized triglycerides, said reactant calculated as a triglyceride constituting about 50 per cent or more thereof.

2. Ester resin according to claim 1 in which the reactant comprises fatty acid from linseed oil.

3. Ester resin according to claim 1 in which the reactant comprises fatty acid from soya bean oil.

4. Ester resin according to claim 1 in which the polyhydric alcohol is glycerol.

5. Ester resin comprising the reaction product of a cyclopentadiene adduct of maleic anhydride with a polyhydric alcohol and a drying oil fatty acid, said fatty acid calculated as a triglyceride constituting about 50 per cent or more thereof.

6. Process of preparing a resinous ester product which comprises heating a cyclopentadiene adduct of maleic anhydride with a polyhydric alcohol to a temperature in the neighborhood of 200° C., adding a reactant selected from the group consisting of fatty acids of drying and semi-drying oils, their monoglycerides and their oxidized triglycerides in proportion when calculated as a triglyceride to form about 50 per cent or more of the mass, and continuing the heating at about 200° C. for a period to cause the formation of a resin in a liquid state.

7. Process of preparing a resinous ester product which comprises heating a cyclopentadiene adduct of maleic anhydride with a polyhydric alcohol and including in the mass a drying oil fatty acid, the adduct and the fatty acid being present in approximately molar proportions and the alcohol in amount to yield a final product having an acid value ranging from about 10 to 90.

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