

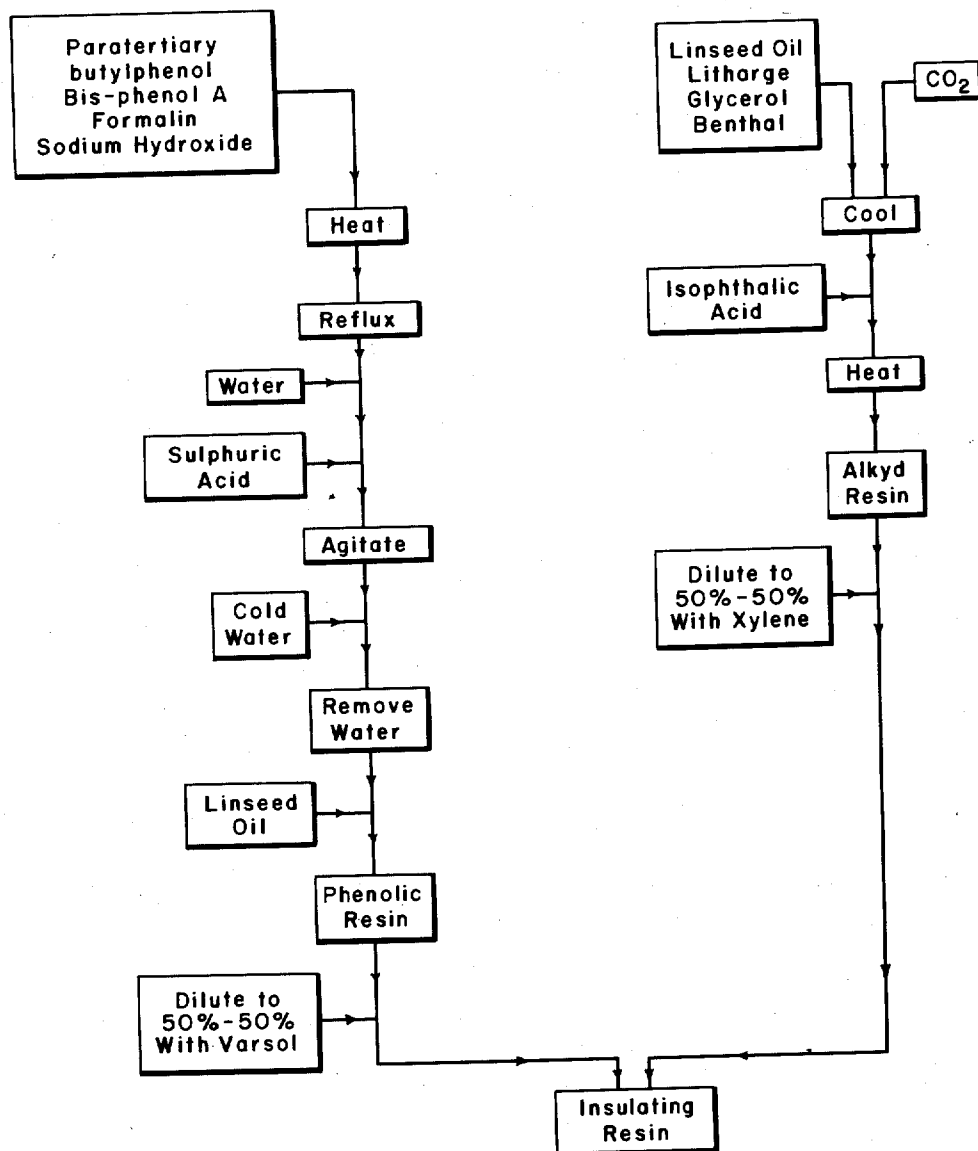
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HEAT RESISTANT ELECTRICAL INSULATING VARNISH

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WITNESSES

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HEAT RESISTANT ELECTRICAL INSULATING
VARNISH

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3 Claims. (Cl. 260—20)

Matter enclosed in heavy brackets [] appears in the
original patent but forms no part of this reissue speci-
fication; matter printed in italics indicates the additions
made by reissue.

This invention relates to the preparation of a heat
resistant electrical insulating varnish and more particu-
larly to an alkyd-phenolic resin heat resistant electrical
insulating varnish.

Alkyd resin and phenolic resin mixtures have been
used heretofore in the electrical industry as electrical
insulating materials. Generally, the alkyd resin com-
ponent has been made by reacting phthalic anhydride,
glycerol, and linseed oil. The alkyd resin so prepared is
satisfactory when combined with a phenolic resin to
form an electrical insulation material for operation in a
temperature range below 105° C. However, when ma-
chinery is operated at a higher temperature, for instance
130° C., this insulation begins to deteriorate rapidly.

The object of this invention is to provide an alkyd-
phenolic resin varnish suitable for use as electrical
insulation at temperatures above 105° C.

Another object of this invention is to provide an alkyd-
phenolic-silicone resin varnish suitable for use as elec-
trical insulation at temperatures above 105° C.

Still another object of the present invention is to pro-
vide electrical insulation suitable for use on machinery
operating consistently above 130° C., comprised of an
admixture of a medium oil length linseed modified
glycerol isophthalate alkyd resin and a short oil length
varnish vehicle consisting of a heat reactive oil soluble
phenolic resin coreacted with maleinized linseed oil.

Other objects of the invention will, in part, be ob-
vious and will, in part, appear hereinafter.

For a more complete understanding of the invention
reference is made to the following description taken
in conjunction with the accompanying drawing, the single
figure of which is a schematic view in diagrammatic
form illustrating one convenient method for preparing
the alkyd-phenolic electrical insulation of this inven-
tion.

In accordance with the present invention and in the
attainment of the foregoing objects there is provided,
broadly, a high temperature electrical insulating varnish
composition comprising in admixture (A) from 25% to
75% by weight of an alkyd resin and (B) from 75%
to 25% by weight of a particular phenolic resin.

The alkyd resin (A) is derived by admixing and
heating to a temperature within the range of 200° C.
to 240° C. (1) at least one dibasic acid selected from
the group consisting of isophthalic and terephthalic acid
with (2) an aliphatic polyhydric alcohol and (3) a
drying oil. The reactants are employed in such pro-
portions that the drying oil constitutes from 40% to
55% by weight of the total weight of alkyd resin. The
reactants are heated until the resin has an acid number
in the range of from 4 to 15.

The phenolic resin (B) is derived by admixing and
heating to a temperature within the range of 70° C. to
reflux (1) from 90 to 80 mol percent of paratertiary
butyl phenol and (2) from 10 to 20 mol percent of di-
phenylol-propane with (3) from 1.5 to 2 mols of an al-
dehyde selected from the group consisting of aqueous

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formaldehyde and polymers of formaldehyde in the pre-
sence of from 0.2% to 5%, based on the weight of the
phenols, of an alkaline catalyst such as alkali metal hy-
droxide. The reaction product then is rendered acidic
with an acid to a pH of between 4 and 7. Water then
is removed from the acidified reaction product by evap-
oration. The product then is maintained at a tem-
perature in the range of 135° C. to 140° C. until it has
a ball and ring softening temperature of 100° C. after
which maleinized linseed oil is added in such proportion
that there is 12 gallons to 25 gallons of maleinized lin-
seed oil to 100 pounds of phenolic resin reaction product.

More specifically in preparing the alkyd resin (A)
predetermined quantities of a suitable (1) drying oil,
(2) an aliphatic polyhydric alcohol, (3) a monobasic
acid and (4) a catalyst are charged into a suitable re-
action vessel and heated to 240° C. in an inert atmos-
phere, for example, carbon dioxide for a period of time
sufficient to insure a substantially complete reaction.

Suitable drying oils include linseed oil, raw linseed
oil, tung oil, oiticica oil, mixtures of the aforesaid oils
and the like. To achieve the necessary flexibility, cure
time, and viscosity, and since the resultant varnish will
be cured by baking rather than air drying, it is critical
that the resultant resin have a medium oil length. There-
fore, the percent of drying oil in the resin should com-
prise 40% to 55% by weight of the total weight of resin.

A suitable aliphatic polyhydric alcohol is any alcohol
containing more than one hydroxy group, for example,
glycerol, propylene glycol, trimethylene glycol, tetra-
methylen glycol, ethylene glycol and the like and mix-
tures of two or more such polyhydric alcohols.

The purpose for employing monocarboxylic acid is
that it yields one hydrogen ion per molecule in solution,
which ion will react with free hydroxyl ions and thereby
prevent premature gelation in the kettle during esterifica-
tion. Examples of suitable monocarboxylic acids in-
clude aromatic acids such as benzoic acid and phenyl-
acetic acid, and aliphatic acids such as, formic acid,
acetic acid, propionic acid, and caproic acid.

A suitable catalyst is any compound capable of pro-
moting esterification between the alcohol and the acid,
for example, litharge, calcium oxide, sodium ethylate
and lithium ricinoleate.

The esterification reaction is carried out in the presence
of an inert gas such as carbon dioxide to prevent oxygen,
which would be present in a normal atmosphere, from
reacting with the drying oil component, which reaction
would result in premature gelation in the reaction ves-
sel.

After the esterification has been carried substantially
to completion, the mixture is cooled while being sparged
with an inert gas, for example, carbon dioxide, and a
predetermined quantity of at least one dibasic acid is
added, the acid being selected from the group consisting
of isophthalic acid and terephthalic acid.

The cooling of the mixture before adding the dibasic
acid is not considered critical to the reaction but is a
precautionary measure to prevent flashing.

The mixture comprising the initial reaction product
and the dibasic acid is then heated slowly to a tempera-
ture of about 240° C. which temperature is maintained
until the resultant mixture has an acid number in the
range of from 4 to 15, preferably from 8 to 10. A higher
acid number may result in the mixture having a cor-
rosive effect on metals with which it might come in con-
tact. A lower acid number would prevent a complete
reaction with the phenolic resin with which the above
described alkyd resin is mixed in accordance with this
invention.

The above described alkyd resin is mixed with a sui-
table organic solvent, either aromatic or aliphatic, or mix-

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tures thereof for example, mineral spirits, naphtha, xylene, toluene, benzene, and the like, the resultant mixture being 50% by weight solids.

In preparing the phenolic resin (B), predetermined quantities of a mixture of phenols composed of from 90 to 80 mol percent of paratertiarybutyl phenol and from 10 to 20 mol percent of diphenylolpropane, and from 1.5 to 2 mols of an aldehyde, per mol of combined phenol are admixed. The aldehyde is selected from the group consisting of aqueous formaldehyde and polymers of formaldehyde. An alkali metal hydroxide catalyst, for example, sodium or potassium hydroxide, then is added and the mixture is heated to a temperature between 70° C. and reflux with agitation for a period of time sufficient to insure substantially complete reaction. There is a substantial amount of water present in the reaction product.

The reaction time is dependent upon two factors, viz., the amount of heat applied and the amount of catalyst present. The quantity of catalyst present may vary from 0.2% to 5% based upon the weight of the phenols. A reaction time of about 3 hours is required with a minimum amount of catalyst and a temperature of about 70° C. The reaction may be completed in about 1 hour by heating to reflux and using at least ½% by weight of the catalyst based on the weight of the phenols.

The reaction product is treated with an acid to reduce the pH of the reaction product to a range of from 4 to 7. Examples of suitable acids for this purpose are oxalic acid, phthalic anhydride, hydrochloric acid, sulfuric acid and phosphoric acid. The acidification is critical since without acidification the reaction product subsequently obtained is unsuitable for admixing with an oil.

After acidification, the reaction product is agitated for about 15 minutes after which it is allowed to stand whereupon an aqueous layer separates out and is withdrawn.

The resinous layer remaining is subjected to vacuum distillation to an absolute pressure of between 1 mm. and about 50 mm. Hg, to remove the water present. The resinous residue is heated during the vacuum distillation until a temperature of from 100° C. to 130° C. is reached. Then the vacuum is broken and, at atmospheric pressure, the temperature is gradually increased to 135° C. to 140° C. and maintained there for a period of time sufficient to produce a resinous product which, when cooled, is hard and brittle and has a softening point of from 75° C. to 105° C. by the ball and ring method.

The resinous product is then mixed with a quantity of maleinized linseed oil in such proportions that the resulting mixture contains 12 to 25 gallons of the maleinized linseed oil per 100 pounds of the resin. The resin may therefore be said to have a short oil length.

The above described oil modified phenolic resin is mixed with a suitable organic hydrocarbon solvent, for example, a petroleum solvent such as naphtha, or an aromatic solvent such as xylol, the resultant mixture being 50% by weight resin and 50% by weight solvent.

The maleinized linseed oil may be prepared by reacting 100 parts by weight of linseed oil with from 3 to 8 parts by weight of maleic anhydride at a temperature of from 240° C. to 270° C. for not more than four hours until an adduct is produced. Then a polyhydric alcohol is added in an amount to provide from 1 to 1.1 hydroxyl groups per mol of maleic anhydride present in the adduct. The polyhydric alcohol should have no other reactive groups than the hydroxyl groups. Suitable examples are glycerol, ethylene glycol, diethylene glycol, pentaerythritol and 1,3 propylene glycol. The mixture with the added polyhydric alcohol is heated at temperatures of from 200° C. to 270° C. for a few hours to esterify the carboxyl groups of the linseed-maleate adduct.

An acid number of from 5 to 12 and a viscosity of from W to Y on the Gardner-Holdt scale is suitable for the glycerol based maleinized linseed oil.

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The alkyd resin (A) solution and phenolic resin (B) solution prepared as described above then are combined to form an electrical insulating varnish suitable for use on equipment operating at temperatures of 105° C. and above for sustained periods of time. The two resins may be combined in the range of 25% to 75% by weight alkyd resin and 75% to 25% by weight phenolic resin. The particular composition selected for use is dependent, of course, upon the equipment to be insulated. The alkyd resin imparts flexibility and heat resistance to the composition and the phenolic resin imparts thermosetting properties and stability. Therefore, if the varnish is to be used on high speed rotors the composition should be comprised of a majority of phenolic resin. On the other hand if it is to be used on stationary equipment or equipment that will be operated at extremely high temperatures the composition should be composed primarily of alkyd resin.

In a modification of this invention, from 0.25% to 0.5% by weight of a dimethyl siloxane resin may be added to the alkyd-phenolic resin mixture to provide improved heat stability. The addition of the siloxane resin has proven most satisfactory when it is desired to coat glass cloth and similar materials with the insulating varnish.

The most satisfactory results have been obtained by utilizing an alkyd modified dimethyl siloxane resin having a phenyl to methyl ratio in the range of 0.6 to 1.2.

The upper range of siloxane resin content is considered critical, since when over 0.5% by weight of siloxane resin is present difficulty is experienced in causing the resin mixture to gel.

The following examples are illustrative of the practice of this invention. All quantities are by weight unless otherwise specified.

EXAMPLE I

About 520 parts of linseed oil (alkali refined), 167 parts of glycerol (98%), 68 parts of benthal (85% benzoic acid and 15% phthalic acid) and 0.5 part of litharge are charged into a closed reaction vessel equipped with an agitator, thermometer, and inert gas sparging tube. A carbon dioxide atmosphere is established in the flask. The mixture is heated to a temperature of 240° C. and this temperature is maintained for about one hour while the mixture is being agitated. The mixture then is cooled to about 200° C. while being sparged with carbon dioxide and about 352 grams of isophthalic acid (98%) is added.

The resultant mixture is then heated slowly to a temperature of about 240° C. and this temperature is maintained until the resultant mixture has an acid number of about 9.

The mixture is then cooled to approximately 200° C., and mixed with xylene to form a solution comprised of 50% by weight solids and having a viscosity of F to G on the Gardner-Holdt scale.

Satisfactory results also can be achieved by substituting terephthalic acid and mixtures of isophthalic and terephthalic acid for the isophthalic acid employed in Example I.

Satisfactory results also can be achieved by substituting raw linseed oil, safflower oil, tung oil, oiticica oil and mixtures of these oils for linseed oil in Example I.

Equally satisfactory results also are obtainable by substituting trimethylol ethane, trimethylol propane or other trihydroxy alcohol for glycerol in Example I.

Satisfactory results can be obtained by substituting calcium oxide, sodium ethylate, lithium ricinoleate for litharge in Example I.

Satisfactory results can be obtained by substituting benzoic acid, phenylacetic acid, and monocarboxylic acids for benthal in Example I.

Satisfactory results can be obtained by varying the drying oil content in Example I, the only requirement being

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that the oil comprise 40% to 55% by weight of the resultant resin.

EXAMPLE II

Into a closed reaction vessel provided with a reflux column and an agitator there is introduced the following:

	Parts
Paratertiary butyl phenol.....	266.3
Bis-phenol A.....	57.8
Formalin (37%).....	258
Sodium hydroxide.....	1.3

The reaction vessel is heated until refluxing started at atmospheric pressure, and heating under reflux is continued for about 1.5 hours. The resulting condensation product is cooled to about 80° C. and 2.8 parts of sulfuric acid (35%) are added to reduce the pH of the mixture to about 5. The mixture is agitated for approximately 15 minutes more, and then the composition is allowed to stand to permit separation of a resinous layer from an aqueous layer. The aqueous layer is removed and the resinous layer is subjected to vacuum distillation to remove substantially all the water therefrom. The vacuum distillation was continued until a temperature of 130° C. for the mass [ws] was reached at a pressure of about 20 mm. of mercury.

Thereafter, the vacuum is broken and further polymerization of the resin is carried out under atmospheric pressure and a temperature of between 130° C. and 140° C. until a softening point of approximately 100° C. is obtained by the ball and ring method.

Approximately 510 parts of maleinized linseed oil are added and the mixture held at 150° C. to a two-inch hot string.

The mixture is then mixed with xylol so that the resulting mixture is comprised of 50% solids.

Satisfactory results can be achieved by substituting paratertiary butyl phenol for the paratertiary butyl phenol plus bis-phenol A of Example II.

Satisfactory results can be achieved by substituting potassium hydroxide for sodium hydroxide in Example II.

Satisfactory results can be achieved by varying the amount of maleinized oil added as long as the amount added is in the range of 12 to 25 gallons of oil per 100 pounds [or] of resin.

EXAMPLE III

Equal parts of the 50% solutions of Example I and Example II were thoroughly mixed to form an electrical insulating varnish. Physical and electrical tests disclosed the following properties:

Viscosity, Demmler #1, seconds, at 25° C.	112
Specific gravity at 25° C.	0.946
Percent solids	49.6
ASTM drying time at 135° C. minutes....	15
Gel time at 135° C. do.....	35
Durometer hardness, 6-hour cake at 135° C.	30-5
Oil Cake after 24-hours at 110° C. in oil	60-50
ASTM oil proofness	Passes
Dielectric strength, VPM:	
Dry	3,050
Wet	2,350
ASTM flex life at 110° (no failure) hours....	3,300
ASTM flex life at 150° C. do.....	264

EXAMPLE IV

Three-tenths of one percent by weight of a cold blending siloxane resin having a phenyl to methyl ratio in the range of 0.6 to 1.2 was added to the high temperature electrical insulating varnish of Example III.

EXAMPLE V

Seventh-tenths of one percent by weight of the siloxane resin of Example IV was added to the high temperature

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electrical varnish of Example III. It was impossible to gel the resulting mixture.

Since certain changes in carrying out the above processes and in the product embodying the invention may be made without departing from its scope, it is intended that the accompanying description and drawing be interpreted as illustrative and not limiting.

We claim as our invention:

1. A high temperature electrical insulating varnish composition comprising in admixture (A) from 25% to 75% by weight of an alkyd resin derived by admixing and heating to a temperature in the range of 200° C. to 240° C. (1) at least one dibasic acid selected from the group consisting of isophthalic acid, terephthalic acid, and methyl esters of terephthalic acid, with (2) an aliphatic polyhydric alcohol and (3) a drying oil, said reactants being employed in such proportions that the drying oil constitutes 40% to 55% by weight of the total weight of alkyd resin, and said alkyd resin being reacted to an acid number in the range of 4 to 15 and [(b)] (B) from 75% to 25% by weight of a phenol resin derived by admixing and heating to a temperature within the range of 70° C. to reflux (1) from 90 to 80 mol percent of paratertiary butyl phenol, (2) from 10 to 20 mol percent of diphenylol propane, and (3) from 1.5 to 2 mols of an aldehyde selected from the group consisting of formaldehyde and polymers of formaldehyde in the presence of from 0.2% to 5% based on the weight of the phenols, of an alkali metal hydroxide, the aqueous reaction product then being neutralized and rendered acidic with an acid to a pH in the range of 4 to 7, removing the water from the acidified reaction product by evacuation, heating and maintaining the product at a temperature of 135° C. to 140° C. until a ball and ring softening temperature of 100° C. is obtained, and then admixing maleinized linseed oil therewith in such proportion that there is [25 gallons to 40 gallons] 12 gallons to 25 gallons of maleinized linseed oil per 100 pounds of reaction product, said maleinized linseed oil being the reaction product of 100 parts of linseed oil and from 3 to 8 parts of maleic anhydride at a temperature of from 240° C. to 270° C. for not more than 4 hours until an adduct is produced, after which an aliphatic polyhydric alcohol is admixed in an amount to furnish from 1 to 1.1 hydroxyl groups for each maleic anhydride molecule present in the adduct, the polyhydric alcohol having no other reactive groups than the hydroxyl groups, and an esterifying reaction between the polyhydric alcohol and the maleic anhydride radicals in the adduct is effected by heating the mixture at a temperature up to 270° C. for at least one hour.

2. A high temperature electrical insulating varnish composition comprising in admixture (A) from 25% to 75% by weight of an alkyd resin derived by admixing and heating to a temperature within the range of 200° C. to 240° C. (1) at least one dibasic acid selected from the group consisting of isophthalic acid and terephthalic acid and methyl esters of terephthalic acid with (2) an aliphatic polyhydric alcohol, (3) a monobasic acid, and (4) a drying oil, said reactants being employed in such proportions that the drying oil constitutes 40% to 55% by weight of the total weight of the alkyd resin, and said alkyd resin having been reacted to an acid number in the range of 4 to 15 and (B) from 75% to 25% by weight of a phenol resin derived by admixing and heating to a temperature within the range of 70° C. to reflux (1) from 90 to 80 mol percent of paratertiary butyl phenol, (2) from 10 to 20 mol percent of diphenylol propane, and (3) from 1.5 to 2 mols of an aldehyde selected from the group consisting of aldehydes and polymers of formaldehyde in the presence of (3) from 0.2% to 5%, based on the weight of the phenols, of an alkali metal hydroxide, the aqueous reaction product then being neutralized and rendered acidic with an acid to a pH in the range of 4 to 7 removing the water from the acidified reaction product by evacuation, heating and maintaining the product of a temperature in the range of

135° C. to 140° C. until a ball and ring softening temperature of 100° C. is obtained, and then admixing maleinized linseed oil in such proportion that there is [25 gallons to 40 gallons] 12 gallons to 25 gallons of maleinized linseed oil per 100 pounds of reaction product, said maleinized linseed oil being the reaction product of 100 parts of linseed oil and from 3 to 8 parts of maleic anhydride at a temperature of from 240° C. to 270° C. for not more than 4 hours until adduct is produced, after which an aliphatic polyhydric alcohol is admixed in an amount to furnish from 1 to 1.1 hydroxyl groups for each maleic anhydride molecule present in the adduct, the polyhydric alcohol having no other reactive groups than the hydroxyl groups, and an esterifying reaction between the polyhydric alcohol and the maleic anhydride radicals in the adduct is effected by heating the mixture at a temperature up to 270° C. for at least one hour.

3. A high temperature electrical insulating varnish composition comprising in admixture (A) from 25% to 75% by weight of an alkyd resin derived by admixing and heating to a temperature in the range of 200° C. to 240° C. (1) at least one dibasic acid selected from the group consisting of isophthalic acid, terephthalic acid, and methyl esters of terephthalic acid, with (2) an aliphatic polyhydric alcohol and (3) a drying oil, said reactants being employed in such proportions that the drying oil constitutes 40% to 55% by weight of the total weight of alkyd resin, and said alkyd resin having been reacted to an acid number in the range of 8 to 10 and (B) from 75% to 25% by weight of a phenol resin derived by admixing and heating to a temperature within the range of 70° C. to reflux (1) from 90 to 80 mol percent of paratertiary butyl phenol, (2) from 10 to 20 mol percent of diphenylol propane, and (3) from 1.5 to 2 mols of an aldehyde selected from the group consist-

ing of aldehydes and polymers of formaldehyde in the presence of from 0.2% to 5% based on the weight of the phenols, of an alkali metal hydroxide, the aqueous reaction product then being neutralized and rendered acidic with an acid to a pH in the range of 4 to 7, removing the water from the acidified reaction product by evacuation, heating and maintaining the product to a temperature in the range of 135° C. to 140° C. until a ball and ring softening temperature of 100° C. is obtained, and then admixed maleinized linseed oil in such proportion that there is [25 gallons to 40 gallons] 12 gallons to 25 gallons of maleinized linseed oil per 100 pounds of reaction product, said maleinized linseed oil being the reaction product of 100 parts of linseed oil and from 3 to 8 parts of maleic anhydride at a temperature of from 240° C. to 270° C. for not more than 4 hours until an adduct is produced, after which an aliphatic polyhydric alcohol is admixed in an amount to furnish from 1 to 1.1 hydroxyl groups for each maleic anhydride molecule present in the adduct, the polyhydric alcohol having no other reactive groups than the hydroxyl groups, and an esterifying reaction between the polyhydric alcohol and the maleic anhydride radicals in the adduct is effected by heating the mixture at a temperature up to 270° C. for at least one hour.

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