

1 METHOD OF PREPARING VEGETABLE OIL-MODIFIED PHENOLIC RESIN
AND LAMINATE PRODUCED BY USING THE SAME

5 BACKGROUND OF THE INVENTION

(a) Field of the Invention

The present invention relates to a method of preparing a vegetable oil-modified phenolic resin useful as
10 a material of paper-phenol laminates and copper-clad laminates (hereinafter, they will be given a general name of "laminate") and to a laminate which is produced by using the vegetable oil-modified phenolic resin and is excellent in low-temperature punching quality.

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(b) Description of the Related Art

Paper-phenol laminates have been pierced or shaped by punching using pierce dies or blank dies. In order to minimize the dimensional change of printed wiring
20 boards, it has become a new tendency to carry out the punching at room temperature without heating, and flexibilized phenolic resins are used for the production of laminates to improve the punching quality of the laminates. The flexibilization of phenolic resins has mainly been
25 performed by using tung oil, which comprises mainly of

1 eleostearic acid and is very reactive, or phosphoric
esters, such as triphenyl phosphate. However, tung oil,
which occur in nature, is inseparable from severe
fluctuation of price and is often hardly available due to
5 natural disasters, such as abnormal weather, floodwater and
earthquake, or artificial factors, so that they are
difficult to supply stably. Also, the flexibilization by
using phosphoric esters causes deterioration in the solvent
resistance and electrical properties of laminates, thereby
10 making it difficult to improve low temperature punching
quality by using phosphoric esters alone.

Some examples of other vegetable oils which have
been examined as the alternatives to tung oil are
linseed oil and soybean oil, which comprise mainly of
15 linoleic acid or linolenic acid. These vegetable oils
however are less reactive with phenols. In order to solve
this problem, it has been proposed to allow such vegetable
oils to react with phenols under severe reaction
conditions, for example, in the presence of large amounts
20 of Lewis acids [Japanese Patent Application Kokai Koho
(laid-open) No. 55-3903 and Japanese Patent Application
Kokai Koho (laid-open) No. 55-108414]. However, the use of
large amounts of Lewis acids also causes hydrolysis of the
vegetable oils and increases low molecular weight
25 components, thereby causing problems in that, after the

1 production of laminates, the low molecular weight
components and unreacted vegetable oils ooze out of the
laminates and the large amounts of catalysts deteriorate
the electrical properties of the laminates.

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SUMMARY OF THE INVENTION

10 In consideration of the stable availability, both
in price and in supply, of the vegetable oils comprising
mainly of linoleic acid or linolenic acid, such as linseed
oil and soybean oil, the inventors thought that these
vegetable oils would be useful for the flexibilization of
laminates if they could be enabled to react with phenols.
15 As the result of study based on the above thought, the
inventors have found that using a small amount of a
perfluorosulfonic acid or an anhydride thereof as a
catalyst makes the vegetable oils comprising mainly of
linoleic acid or linolenic acid to react with phenols
20 efficiently without causing the hydrolysis of these
vegetable oils, and they have consequently completed the
present invention.

That is, the present invention provides a method
of preparing a vegetable oil-modified phenolic resin,
25 comprising allowing a phenol to react with a non-conjugated

1 drying oil in the presence of a super acid selected from
the group consisting of a perfluorosulfonic acid, a
perfluorosulfonic anhydride and a mixture thereof to form a
phenol-added vegetable oil, and allowing the phenol-added
5 vegetable oil to react with an aldehyde in the presence of
an alkaline catalyst under weakly alkaline conditions to
form a vegetable oil-modified phenolic resin.

The present invention further provides a laminate
comprising plural sheets of paper impregnated with a
10 cured product of the vegetable oil-modified phenolic resin.

In the method of the present invention, the use
of a specific catalyst, namely a perfluorosulfonic acid or
an anhydride thereof, enables even vegetable oils
comprising mainly of linoleic acid or linolenic acid to
15 react with phenols without causing hydrolysis of the
vegetable oils to low molecular weight components.
Further, since even a small amount of the catalyst
functions sufficiently, the resulting vegetable oil-
modified phenolic resin does not deteriorate the electrical
20 properties of laminates. When phenol-added vegetable oils
prepared according to the present invention were allowed to
react with formaldehyde, and laminates were produced by
impregnating paper with the obtained varnish, laminating
the impregnated paper and compression molding the laminated
25 composite, no low molecular weight components oozed out of

the obtained laminates, and the electrical properties of the laminates were not deteriorated. This shows that the conventional problems are solved.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The non-conjugated drying oil used in the present invention is a vegetable oil comprising mainly of linoleic acid or linolenic acid and may be a drying oil with an iodine value of more than 130 or a semi-drying oil with an iodine value of 100 to 130. Some examples of the non-conjugated drying oil include linseed oil, safflower oil, soybean oil, sesame oil, perilla oil, hempseed oil and cotton seed oil. Among these, the preferred examples are linseed oil and soybean oil which are inexpensive and can be supplied stably. In particular, linseed oil is preferable because of its high degree of unsaturation. These non-conjugated drying oils may be used individually or in a combination of two or more of them.

Some examples of the phenol which may be used in the present invention include phenol, o-cresol, m-cresol, p-cresol, xlenols, catecol, resorcin, hydroquinone, octylphenols, tert-butylphenols, nonylphenols and bisphenol A. These phenols may be used individually or in a -----

1 combination of two or more of them.

In the present invention, a super acid selected from the group consisting of a perfluorosulfonic acid and a perfluorosulfonic anhydride and a mixture thereof is used
5 as a catalyst for catalyzing the reaction of the phenol and the non-conjugated drying oil. Some examples of the super acid include fluorosulfonic acid, fluorosulfonic anhydride, trifluoromethanesulfonic acid, trifluoromethanesulfonic anhydride, pentafluoroethanesulfonic acid,
10 pentafluoroethanesulfonic anhydride, heptafluoropropanesulfonic acid, heptafluoropropanesulfonic anhydride, nonafluorobutanesulfonic acid, nonafluorobutanesulfonic anhydride, undecafluoropentanesulfonic acid and
15 undecafluoropentanesulfonic anhydride. The preferred examples are fluorosulfonic acid, trifluoromethanesulfonic acid and trifluoromethanesulfonic anhydride. These super acids may be used individually or in a combination of two or more of them.

20 Although the ratio of the non-conjugated drying oil to the phenol is not particularly limited, the non-conjugated drying oil and the phenol are preferably used in a non-conjugated drying oil:phenol weight ratio of from 2:8 to 6:4, more preferably from 3:7 to 4:6, in order to
25 improve the properties of laminates highly effectively. If

1 the ratio of the non-conjugated drying oil to the phenol is
more than 6:4, curing of the vegetable oil-modified
phenolic resin in laminates may be insufficient so as to
make the surface of the laminates tacky. If the ratio is
5 less than 2:8, the low temperature punching quality of
laminates may be insufficient.

Although the amount of the super acid used for
the reaction of the non-conjugated drying oil with the
phenol is not particularly limited, it is preferable to use
10 1 to 0.01 part by weight, particularly 0.01 to 0.5 parts by
weight of the super acid per 100 parts by weight of the
non-conjugated drying oil. If the amount of the super acid
is more than 1 part by weight, the electrical properties of
laminates may be deteriorated, and if it is less than 0.01
15 part by weight, the reaction may slow down and the
industrial productivity may be decreased.

The reaction of the non-conjugated drying oil and
the phenol may be carried out in the absence or presence of
solvents. In consideration of the following reaction with
20 an aldehyde, the reaction is preferably carried out in the
absence of solvents. The reaction temperature of the
reaction is generally 50 to 200 °C. If the reaction
temperature is too high, hydrolysis may occur to generate
low molecular weight components, thereby deteriorating the
25 properties of laminates. In order to inhibit the

1 generation of low molecular weight components, a reaction
temperature of 50 to 120 °C is particularly preferable.

At the time of the reaction of the non-conjugated
drying oil and the phenol, xylene resin may be added
5 according to demand. Adding the xylene resin further
improves the resistance to alkalis and the electrical
properties of laminates.

After the completion of the reaction of the non-
conjugated drying oil and the phenol, the phenol-added
10 vegetable oil obtained is allowed to react with an aldehyde
in the presence of an alkaline catalyst under weakly
alkaline conditions to form resol, namely a vegetable oil-
modified phenolic resin. At the time of the reaction for
forming the resol, a phenol may be added. The kind of the
15 phenol added may be identical with or different from that
of the phenol used for the above reaction with the non-
conjugated drying oil.

After the completion of the reaction for forming
the phenol-added vegetable oil, the phenol-added vegetable
20 may be separated from the reaction solution, or the
reaction solution containing the phenol-added vegetable oil
may be used for the reaction for forming resol by adding
the aldehyde, the alkaline catalyst and, according to
demand, the phenol directly to the reaction solution.

25 Some examples of the aldehyde which may be used

1 in the present invention include formaldehyde, formalin,
acetaldehyde, paraformaldehyde and hexamethylenetetramine.
These aldehydes may be used individually or in a
combination of two or more of them.

5 The amount of the aldehyde calculated as
formaldehyde is generally 1.1 to 1.6 moles, preferably 1.2
to 1.5 moles, per one mole of the total phenol used in the
method of the present invention. If the amount of the
aldehyde is less than 1.1 moles or more than 1.6 moles, the
10 punching quality of laminates may be deteriorated.

Some examples of the alkaline catalyst which may
be used for the reaction for forming resol include ammonia,
trimethylamine, triethylamine and triethanolamine. These
alkaline catalysts may be used individually or in a
15 combination of two or more of them. The amount of the
alkaline catalyst is generally 0.03 to 0.2 moles,
preferably 0.05 to 0.1 moles, per mole of the phenol. If
the amount of the alkaline catalyst is less than 0.03
moles, the reaction may take a long time, and curability of
20 the product vegetable oil-modified phenolic resin may be
deteriorated, thereby deteriorating the properties of
laminates. If it is more than 0.2 moles, the vegetable
oil-modified phenolic resin may have an increased molecular
weight, which may cause difficulty in impregnation, thereby
25 deteriorating the properties of laminates.

1 The reaction temperature of the reaction for
forming resol is generally 1 to 5 hours, preferably about 2
hours.

 The reaction for forming resol may be carried out
5 in the absence of solvents, or in the presence of a
solvent, such as methanol, acetone or methyl ethyl ketone.

 The method of separating the resulting vegetable
oil-modified phenolic resin after the completion of the
reaction for forming resol is not particularly limited, and
10 an appropriate method is to dehydrate and concentrate the
reaction solution at 40 to 90 °C under reduced pressure.

 The laminate of the present invention may be
produced by laminating plural sheets of paper impregnated
with the vegetable oil-modified phenolic resin and molding
15 the resulting laminate with heat and pressure.

 In the production of the laminate of the present
invention, first an organic solvent, such as toluene or
methanol, is added under atmospheric pressure to the
vegetable oil-modified phenolic resin obtained in the
20 manner as described above, to form varnish. Paper is
impregnated with the varnish, and the impregnated paper is
then freed of solvent by heating to obtain a prepreg. A
desired number of the prepreg are laminated to form a
laminated composite, which is then molded by heating and
25 pressing to form a laminate. When the laminated composite

1 further has a layer of metal foil, such as copper foil, on
one or each side thereof, a metal-clad laminate is produced
by heating and pressing the laminate composite. The metal
foil may be coated with an adhesive on one side coming into
5 contact with the prepreg.

To the varnish of the vegetable oil-modified
phenolic resin may be added various additives, for example,
flame retardants which are generally added to phenolic
resins, such as bromo-type flame retardants, phosphorus-
10 type flame retardants, nitrogen-type flame retardants and
antimony-type flame retardants.

Examples of the paper which may be used in the
present invention include cotton paper, linter paper, kraft
paper and rayon paper. These paper may be used
15 individually or in a combination of two or more of them.

Prior to the production of the laminate of the
present invention, the paper may be impregnated with a
water-soluble phenolic resin. Paper impregnated with
water-soluble phenolic resins can be easily impregnated
20 with the varnish of the vegetable oil-modified phenolic
resin. The water-soluble phenolic resin can be dissolved
completely in water or in a solvent mixture of water and
alcohols. Some examples of the water-soluble phenolic
resin include those obtained by allowing a phenol, such as
25 phenol, a cresol, a xylenol, catecol, resorcin or a

1 nonylphenol, to react with 1 to 3 moles of formaldehyde per
mole of the phenol, in the presence of a catalyst, for
example, an organic tertiary amine, such as trimethylamine,
triethylamine or triethanolamine, or an alkaline or
5 alkaline earth metal hydroxide, such as potassium
hydroxide, sodium hydroxide, calcium hydroxide, barium
hydroxide or magnesium hydroxide, at 40 to 90 °C .

Hereinafter, the present invention will be
described in detail referring to the following Examples.

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EXAMPLES 1 TO 5, REFERENCE EXAMPLE 1
AND COMPARATIVE EXAMPLES 1 AND 2

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EXAMPLE 1

Synthesis of a varnish for the preparation of laminates

In a two-liter three neck flask equipped with a
thermometer and a condenser tube were introduced 200 g of
20 linseed oil, 200 g of phenol and 0.3 g of
trifluoromethanesulfonic acid, and were then allowed to
react at 80 °C for three hours. After the completion of
the reaction, thereto were added 180 g of phenol, 255 g of
paraformaldehyde, 80 g of methanol and 38 g of 25 % aqueous
25 ammonia and were then allowed to react at 80 °C to form

1 resol. During the reaction, sampling was carried out to
determine the gelation time of the reaction mixture at 160
°C. When the gelation time of the reaction mixture at 160
°C decreased to 6 minutes, the reaction mixture was
5 dehydrated and concentrated by heating at 80 °C under
reduced pressure. When the gelation time of the reaction
mixture decreased to three minutes, the reaction was
terminated, and 200 g of toluene and 200 g of methanol were
added to the reaction mixture to form a varnish.

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EXAMPLE 2

Synthesis of a varnish for the preparation of laminates

In the same flask as that used in Example 1 were
15 introduced 200 g of linseed oil, 250 g of a mixture of m-
cresol and p-cresol and 1.0 g of fluorosulfonic acid, and
were then allowed to react at 90 °C for two hours. Thereto
was added 50 g of a xylene resin (Trade name: NIKANOL-H,
produced by Mitsubishi Gas Chemical Co., Inc.), and the
20 mixture was allowed to react at 90 °C for one hour.
Subsequently, thereto were added 100 g of phenol, 177 g of
paraformaldehyde, 60 g of methanol and 21.6 g of 25 %
aqueous ammonia, to carry out a reaction for forming resol
at 80 °C. When the gelation time of the reaction mixture
25 at 160 °C decreased to 6 minutes, the reaction mixture was

1 dehydrated and concentrated by heating at 80 °C under
reduced pressure. When the gelation time decreased to
three minutes, the reaction was terminated, and 200 g of
toluene and 200 g of methanol were added to the reaction
5 mixture to form a varnish.

EXAMPLE 3

Synthesis of a varnish for the preparation of laminates

10 In the same flask as that used in Example 1 were
introduced 200 g of phenol, 50 g of a xylene resin (Trade
name: NIKANOL-H, produced by Mitsubishi Gas Chemical Co.,
Inc.) and 1.0 g of trifluoromethanesulfonic acid, and were
then allowed to react at 100 °C for one hour. Thereto was
15 added 200 g of soybean oil, and the reaction mixture was
then allowed to react at 100 °C for 5 hours. Subsequently,
thereto were added 180 g of phenol, 255 g of
paraformaldehyde, 80 g of methanol and 38 g of 25 % aqueous
ammonia, and the reaction mixture was then allowed to react
20 at 80 °C to form resol. When the gelation time of the
reaction mixture at 160 °C decreased to 6 minutes, the
reaction mixture was dehydrated and concentrated by heating
at 80 °C under reduced pressure. When the gelation time
decreased to three minutes, the reaction was terminated,
25 and 200 g of toluene and 200 g of methanol was then added

1 to the reaction mixture to form a varnish.

EXAMPLE 4

5 Synthesis of a varnish for the preparation of laminates

A varnish was synthesized by the same procedure as that of Example 1 with the exception that 0.3 g of trifluoromethanesulfonic anhydride was used as a catalyst in place of the trifluoromethanesulfonic acid used in
10 Example 1.

EXAMPLE 5

Synthesis of a varnish for the preparation of laminates

15 A varnish was synthesized by the same procedure as that of Example 2 with the exception that 1.0 g of trifluoromethanesulfonic anhydride was used as a catalyst in place of the fluorosulfonic acid used in Example 2.

20 COMPARATIVE EXAMPLE 1

Synthesis of a varnish by a conventional method

In the same flask as that used in Example 1 were introduced 200 g of linseed oil, 250 g of a mixture of m-cresol and p-cresol and 1.0 g of p-toluenesulfonic acid,
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1 and were then allowed to react at 90 °C for two hours.
Thereto was added 50 g of a xylene resin (Trade name:
NIKANOL-H, produced by Mitsubishi Gas Chemical Co., Inc.),
and the reaction mixture was allowed to react at 90 °C for
5 one hour. Subsequently, thereto were added 100 g of
phenol, 177 g of paraformaldehyde, 60 g of methanol and
21.6 g of 25 % aqueous ammonia, and the reaction mixture
was then allowed to react at 80 °C to form resol. When a
sample of the reaction mixture was placed on a plate heated
10 to 160 °C to determine gelation time, the sample separated
into gel and oil. After the reaction was carried out for 7
hours, the reaction mixture was dehydrated and concentrated
by heating at 80 °C under reduced pressure. When the
distillation of distillates stopped, 200 g of toluene and
15 200 g of methanol were added to the reaction mixture to
form a comparative varnish.

REFERENCE EXAMPLE 1

20 Synthesis of tung oil-modified phenolic resin

In the same flask as that used in Example 1 were
introduced 200 g of phenol, 50 g of a xylene resin (Trade
name: NIKANOL-H, produced by Mitsubishi Gas Chemical Co.,
Inc.) and 1.0 g of p-toluenesulfonic acid, and were then
25 allowed to react at 100 °C for one hour. Thereto was added

1 200 g of tung oil, and the reaction mixture was then
allowed to react at 100 °C for 5 hours. After the
completion of the reaction, 180 g of phenol, 255 g of
paraformaldehyde, 80 g of methanol and 38 g of 25 % aqueous
5 ammonia, and the reaction mixture was then allowed to react
at 80 °C to form resol. When gelation time at 160 °C
decreased to 6 minutes, the reaction mixture was dehydrated
and concentrated by heating at 80 °C under reduced
pressure. When gelation time decreased to three minutes,
10 the reaction was terminated, and 200 g of toluene and 200 g
of methanol were added to the reaction mixture to form a
varnish.

COMPARATIVE EXAMPLE 2

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Synthesis of a linseed oil-modified phenolic resin by using
a Lewis acid catalyst

In the same flask as that used in Example 1 were
introduced 200 g of phenol, 200 g of linseed oil and 3 g of
20 aluminum chloride, and were then allowed to react at 100 °C
for three hours. Thereto were added 180 g of phenol, 255 g
of paraformaldehyde, 80 g of methanol and 38 g of 25 %
aqueous ammonia, and the reaction mixture was then allowed
to react at 80 °C to form resol. When gelation time at 160
25 °C decreased to 6 minutes, the reaction mixture was

1 dehydrated and concentrated by heating at 80 °C under
reduced pressure. When gelation time decreased to three
minutes, the reaction was terminated, and 200 g of toluene
and 200 g of methanol were added to the reaction mixture to
5 form a comparative varnish.

PRODUCTION OF LAMINATES

After each varnish thus obtained was adjusted to
10 a resin content of 48 % by weight, kraft paper pre-
impregnated with a water-soluble phenolic resin, which was
prepared by allowing one mole of phenol to react with three
moles of formaldehyde in the presence of trimethylamine at
60 °C for 8 hours, was impregnated with the varnish and was
15 then dried, to obtain a prepreg of a vegetable oil-modified
phenolic resin. A predetermined number of the prepreg and
copper foil coated with an adhesive were laminated so that
the copper foil formed an outermost layer of the laminated
composite. The laminated composite was heated and pressed
20 for one hour at a pressure of 100 kg/cm² and a temperature
of 160 °C, to obtain a single-sided copper-clad laminate.
The insulation resistance, soldering heat resistance and
solvent resistance of the obtained laminates were measured
in accordance with JIS-C 6481, and the punching quality of
25 the laminates was measured in accordance with ASTM D-617.

- 1 The results are listed in Table 1. The contents of low
molecular weight components which were generated in the
reaction of vegetable oils and phenols and were contained
in the vegetable oil-modified phenolic resin were measured
5 by a liquid chromatography, and the results are listed in
Table 1.

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TABLE 1-1

	Conditions	Unit	Ex. 1	Ex. 2	Ex. 3
5	Insulation	A	8.2×10^{12}	7.4×10^{12}	4.3×10^{12}
	resistance	D-2/100	2.7×10^8	3.1×10^8	2.5×10^8
	Soldering				
	heat	A	42	39	36
	resistance	sec			
10	Resistance	In	No abnor-	No abnor-	No abnor-
	to	boiling	mality	mality	mality
	trichloro-	trichloro-	for	for	for
	ethylene	ethylene	30 min	30 min	30 min
	Punching		good at	good at	good at
	quality		40 °C	40 °C	70 °C
15	Content of	%	3	4	7
	low				
	molecular				
	weight				
	components				

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TABLE 1-2

	Conditions	Unit	Ex. 4	Ex. 5	Com. Ex. 1
5	Insulation	A	3.4×10^{13}	2.1×10^{13}	3.8×10^{10}
	resistance	D-2/100	1.6×10^9	9.6×10^8	6.4×10^8
	Soldering				
	heat	A	29	35	2
	resistance				
10	Resistance	In	No abnor-	No abnor-	Surface
	to	boiling	mality	mality	whitening
	trichloro-	trichloro-	for	for	in
	ethylene	ethylene	30 min	30 min	one min
	Punching		Good at	Good at	Bulging
	quality		40 °C	40 °C	
15	Content of	%	4	5	3
	low				
	molecular				
	weight				
	components				

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TABLE 1-3

	Conditions		Unit	Ref. Ex. 1	Com. Ex. 2
5	Insulation	A	Ω	5.9×10^{12}	5.1×10^{10}
	resistance	D-2/100	Ω	5.7×10^8	2.4×10^8
	Soldering				
	heat	A	sec	45	16
	resistance				
	Resistance	In		No abnor-	Surface
10	to	boiling		mality	whitening
	trichloro-	trichloro-		for	in
	ethylene	ethylene		30 min	one min
	Punching			Good at	Bulging *
	quality			40 °C	
	Content of		%	5	28
	low				
15	molecular				
	weight				
	components				

Bulging * : Fine delamination around holes

1 As apparent from the results listed in Table 1,
the copper-clad laminates that were produced by using the
vegetable oil-modified phenolic resins prepared in Examples
1 to 5 are excellent in insulation resistance, soldering
5 heat resistance, solvent resistance and punching quality,
which stand comparison with those of the copper-clad
laminate that was produced by using the phenolic resin
prepared in Reference Example 1 by using expensive tung
oil. Further, the vegetable oil-modified phenolic resins
10 prepared in Examples 1 to 5 have contents of low molecular
weight components which are as small as that of the tung
oil-modified phenolic resin prepared in Reference Example
1. This means that the catalyst used in the present
invention effectively catalyzes the reaction of non-
15 conjugated drying oils with phenols without causing the
hydrolysis of the non-conjugated drying oils, and that the
phenolic-added vegetable oil resulting from the above
reaction effectively flexibilizes phenolic resins. To the
contrary, the insulation resistance, soldering heat
20 resistance, solvent resistance and punching quality of the
laminates that were produced by using the vegetable oil-
modified phenolic resins prepared in Comparative Examples 1
and 2 by using conventional catalysts were inferior to
those of the laminates of the present invention.
25 Particularly, the vegetable oil-modified phenolic resin

1 prepared in Comparative Example 2 by using a Lewis acid
contains a very large amount of low molecular weight
components. This means that the Lewis acid used in
Comparative Example 2 caused hydrolysis of linseed oil.

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CLAIMS:

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1. A method of preparing a vegetable oil-modified phenolic resin, comprising allowing a phenol to react with a non-conjugated drying oil in the presence of a super acid selected from the group consisting of a perfluorosulfonic acid, a perfluorosulfonic anhydride and a mixture thereof to form a phenol-added vegetable oil, and allowing the phenol-added vegetable oil to react with an aldehyde in the presence of an alkaline catalyst under weakly alkaline conditions to form a vegetable oil-modified phenolic resin.

2. The method as claimed in claim 1, wherein the reaction of the phenol-added vegetable oil with the aldehyde is carried out in the presence of a phenol and the alkaline catalyst under weakly alkaline conditions.

3. The method as claimed in claim 2, wherein the phenol used in the reaction of the phenol-added vegetable oil is selected from the group consisting of phenol, a cresol, a xylenol, catechol, resorcin, hydroquinone, an octylphenol, a tert-butylphenol, a nonylphenol, bisphenol A and a mixture thereof.

4. The method as claimed in claim 1, wherein the



reaction of the phenol with the non-conjugated drying oil is carried out in the presence of a xylene resin and the super acid.

5. The method as claimed in claim 1, wherein the non-conjugated drying oil is selected from the group consisting of linseed oil, safflower oil, soybean oil, sesame oil, perilla oil, hempseed oil, cotton seed oil and a mixture thereof, the super acid is selected from the group consisting of fluorosulfonic acid, fluorosulfonic anhydride, trifluoromethanesulfonic acid, trifluoromethanesulfonic anhydride, pentafluoroethanesulfonic acid, pentafluoroethanesulfonic anhydride, heptafluoropropanesulfonic acid, heptafluoropropanesulfonic anhydride, nonafluorobutanesulfonic acid, nonafluorobutanesulfonic anhydride, undecafluoropentanesulfonic acid, undecafluoropentanesulfonic anhydride and a mixture thereof.

6. The method as claimed in claim 5, wherein the non-conjugated drying oil is selected from the group consisting of linseed oil, soybean oil and a mixture thereof, and the super acid is selected from the group consisting of trifluoromethanesulfonic acid.



1 trifluoromethanesulfonic anhydride, fluorosulfonic acid and
a mixture thereof.

7. The method as claimed in claim 5, wherein the
5 non-conjugated drying oil and the phenol are used in a non-
conjugated drying oil:phenol weight ratio of from 2:8 to
6:4, and the super acid is used in an amount of from 1 to
0.01 part by weight per 100 parts by weight of the non-
conjugated drying oil.

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8. The method as claimed in claim 7, wherein the
phenol is selected from the group consisting of phenol, a
cresol, a xylenol, catecol, resorcin, hydroquinone, an
octylphenol, a tert-butylphenol, a nonylphenol, bisphenol A
15 and a mixture thereof, the aldehyde is selected from the
group consisting of formaldehyde, formalin, acetaldehyde,
paraformaldèhyde, hexamethylenetetramine and a mixture
thereof, and the alkaline catalyst is selected from the
group consisting of ammonia, trimethylamine, triethylamine,
20 triethanolamine and a mixture thereof.

9. The method as claimed in claim 8, wherein the
non-conjugated drying oil is linseed oil or soybean oil,
the phenol is selected from the group consisting of phenol,
25 m-cresol, p-cresol and a mixture thereof, the super acid is



1 selected from the group consisting of
trifluoromethanesulfonic acid, trifluoromethanesulfonic
anhydride and fluorosulfonic acid, the aldehyde is
paraformaldehyde, and the alkaline catalyst is ammonia.

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10. The method as claimed in claim 9, wherein the
reaction of the phenol-added vegetable oil with the
aldehyde is carried out in the presence of a phenol and the
alkaline catalyst under weakly alkaline conditions.

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11. The method as claimed in claim 10, wherein the
reaction of the phenol with the non-conjugated drying oil
is carried out in the presence of a xylene resin and the
super acid.

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12. A laminate comprising a plural sheets of paper
impregnated with a cured product of the vegetable oil-
modified phenolic resin prepared by the method of claim 1.

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13. The laminate of claim 12 further comprising a
sheet of metal foil on a side of the laminate.

14. The laminate of claim 13, wherein the metal foil
is copper foil.

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15. The method as claimed in claim 1, wherein the non-conjugated drying oil is selected from the group consisting of linseed oil, safflower oil, soybean oil, sesame oil, perilla oil, hempseed oil, cotton seed oil and a mixture thereof.