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(54) **Title:** SYNTHESIS OF NAPHTHOL NOVOLAC

(57) **Abstract:** Provided is a method for making naphthol novolac comprising, consisting of, or consisting essentially of: contacting a) a naphthol component comprising i) from 1 to 99 weight percent 1-naphthol; and ii) from 1 to 99 weight percent 2-naphthol; and b) an aldehyde in a reaction zone under reaction conditions to form the naphthol novolac. Also disclosed is curable composition comprising, consisting of, or consisting essentially of: a) an epoxy resin; and b) a hardener component comprising i) an oligomeric compound comprising a phosphorus composition which is the reaction product of an etherified resole with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, and ii) a naphthol novolac prepared by the above method. The curable composition can be used to prepare prepreps and electrical laminates.



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SYNTHESIS OF NAPHTHOL NOVOLAC

FIELD OF THE INVENTION

The present invention is related to epoxy resin compositions. More particularly, the
5 present invention is related to halogen-free or substantially halogen-free formulations.

INTRODUCTION

Epoxy resins are widely used in coatings, adhesives, printed circuit boards,
semiconductor encapsulants, adhesives and aerospace composites thanks to the excellent
10 mechanical strength; chemical, moisture, and corrosion resistance; good thermal, adhesive,
and electrical properties. Naphthol novolac (NPN) has been used as an epoxy hardener for
electrical laminate applications. The use of NPN can also greatly improve flame resistance
and allows for a reduction in the amount of flame retardant used. However, NPN has a high
production cost and poor prepreg appearance which is attributed to high system viscosity.
15 Therefore, a process to produce NPN that avoids these negative aspects would be desirable.

SUMMARY

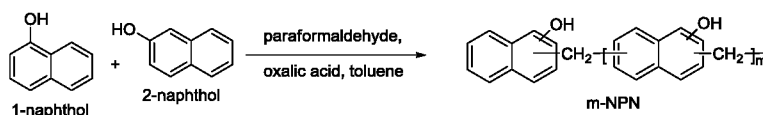
The instant invention is a method for making naphthol novolac comprising, consisting
of, or consisting essentially of: contacting a) a naphthol component comprising i) from 1 to
20 99 weight percent 1-naphthol; and ii) from 1 to 99 weight percent 2-naphthol; and b) an
aldehyde
in a reaction zone under reaction conditions to form the naphthol novolac.

The instant invention is also a curable composition comprising, consisting of, or
consisting essentially of: a) an epoxy resin; and b) a hardener component comprising i) an
25 oligomeric compound comprising a phosphorus composition which is the reaction product of
an etherified resole with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, and ii) a
naphthol novolac prepared by the above method.

DETAILED DESCRIPTION

The instant invention is a method for making a naphthol novolac. The instant invention is a method comprising, consisting of, or consisting essentially of contacting a) a naphthol component comprising i) from 1 to 99 weight percent 1-naphthol; and ii) from 1 to 99 weight percent 2-naphthol; and b) an aldehyde in a reaction zone under reaction conditions to form the naphthol novolac. The reaction conditions can include a reaction temperature in the range of from 80°C to 160°C and a reaction time in the range of from 3 to 72 hrs.

In various embodiments, a naphthol component is contacted with paraformaldehyde to form naphthol novolac. An example of the reaction scheme is depicted in Formula 1, below. The naphthol novolac product is depicted as modified naphthol novolac (m-NPN).



Formula 1

In an embodiment, paraformaldehyde can be used as the aldehyde. Other aldehydes that can be used include, but are not limited to formaldehyde, aliphatic aldehydes, and aromatic aldehydes.

In various embodiments, the naphthol component can be added to a solvent before contact with the aldehyde. Any suitable solvent can be used such as, for example, toluene and xylene.

The reaction conditions include a reaction temperature in the range of from 80°C to 160°C. All individual ranges and subranges from 80°C to 160°C are included herein and disclosed herein, for example, the reaction temperature can be from a lower limit of 80°C, 90°C, 105°C, or 118°C to an upper limit of 90°C, 122°C, 135°C, 144°C, 153°C, or 160°C.

The reaction conditions also include a reaction time in the range of from 3 to 72 hours. All individual ranges and subranges from 3 hours to 72 hours are included herein and disclosed herein, for example, the reaction time can be from a lower limit of 3 hours, 6.5 hours, 8 hours, or 10 hours to an upper limit of 18 hours, 22 hours, 24 hours, 36 hours, 48 hours, and 72 hours.

In other embodiments, the instant invention is a curable composition. The instant invention is a curable composition comprising, consisting of, or consisting essentially of a) an epoxy resin; and b) a hardener component comprising i) an oligomeric compound comprising

a phosphorus composition which is the reaction product of an etherified resole with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, and ii) a naphthol novolac prepared by the above method. The curable composition can further include optionally a filler. The curable composition can further include optionally a catalyst.

5 The curable composition comprises an epoxy resin and a hardener, as described in further details hereinbelow.

 The curable composition may further include one or more fillers. The curable composition may comprise 10 to 80 percent by weight of one or more fillers. All individual values and subranges from 10 to 80 weight percent are included herein and disclosed herein,
10 for example, the weight percent of filler can be from a lower limit of 10, 12, 15, 20, or 25 weight percent to an upper limit of 62, 65, 70, 75, or 80 weight percent. For example, curable composition may comprise 15 to 75 percent by weight of one or more fillers; or in the alternative, curable composition may comprise 20 to 70 percent by weight of one or more fillers. Such fillers include, but are not limited to natural silica, fused silica, alumina,
15 hydrated alumina, and combinations thereof.

 The curable composition may further include one or more catalysts. The curable composition may comprise 0.01 to 50 percent by weight of one or more catalysts. All individual values and subranges from 0.01 to 50 weight percent are included herein and disclosed herein, for example, the weight percent of catalyst can be from a lower limit of 0.01,
20 0.03, 0.05, 0.07, or 1 weight percent to an upper limit of 2, 6, 10, 15, or 50 weight percent. For example, curable composition may comprise 0.05 to 10 percent by weight of one or more catalysts; or in the alternative, curable composition may comprise 0.05 to 2 percent by weight of one or more catalysts. Such catalysts include, but are not limited to 2-methyl imidazole (2MI), 2-phenyl imidazole (2PI), 2-ethyl-4-methyl imidazole (2E4MI), 1-benzyl-2-
25 phenylimidazole (1B2PZ), boric acid, triphenylphosphine (TPP), tetraphenylphosphonium-tetraphenylborate (TPP-k) and combinations thereof.

 The curable composition may further include one or more tougheners. The curable composition may comprise 0.01 to 70 percent by weight of one or more tougheners. All individual values and subranges from 0.01 to 70 weight percent are included herein and
30 disclosed herein, for example, the weight percent of toughener can be from a lower limit of 0.01, 0.05, 1, 1.5, or 2 weight percent to an upper limit of 15, 30, 50, 60, or 70 weight percent. For example, curable composition may comprise 1 to 50 percent by weight of one or more tougheners; or in the alternative, curable composition may comprise 2 to 30 percent by weight of one or more tougheners.

Such tougheners include, but are not limited to core shell rubbers. A core shell rubber is a polymer comprising a rubber particle core formed by a polymer comprising an elastomeric or rubbery polymer as a main ingredient and a shell layer formed by a polymer graft polymerized on the core. The shell layer partially or entirely covers the surface of the rubber particle core by graft polymerizing a monomer to the core. Generally the rubber particle core is constituted from acrylic or methacrylic acid ester monomers or diene (conjugated diene) monomers or vinyl monomers or siloxane type monomers and combinations thereof. The toughening agent may be selected from commercially available products; for example, Paraloid EXL 2650A, EXL 2655, EXL2691 A, each available from The Dow Chemical Company, or Kane Ace® MX series from Kaneka Corporation, such as MX 120, MX 125, MX 130, MX 136, MX 551, or METABLEN SX-006 available from Mitsubishi Rayon.

The curable composition comprises a) an epoxy resin; and b) a hardener component comprising i) an oligomeric compound comprising a phosphorus composition which is the reaction product of an etherified resole with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, and ii) naphthol novolac.

The curable composition may comprise 10 to 90 percent by weight of one or more epoxy resins. All individual values and subranges from 10 to 90 weight percent are included herein and disclosed herein, for example, the weight percent of epoxy resin can be from a lower limit of 12, 17, 20, 30, or 35 weight percent to an upper limit of 55, 70, 86, 90, or 98 weight percent. For example, curable composition may comprise 20 to 98 percent by weight of one or more epoxy resins or in the alternative, curable composition may comprise 30 to 90 percent by weight of one or more epoxy resins. In various embodiments, the epoxy resin is a multifunctional epoxy which has more than two epoxy functionalities. Such epoxy resins include, but are not limited to epoxy resins obtained by glycidifying the condensation product of a phenol or a naphthol with an aldehyde, such as naphthol novolac epoxies, epoxy resins obtained by glycidifying the co-condensation product of naphthol, phenol, and formaldehyde, bisphenol-A novolac epoxies, bisphenol-F novolac epoxies and combinations thereof.

The present invention curable composition includes at least one epoxy resin. The epoxy resin may be saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic and may be substituted. The epoxy resin may also be monomeric or polymeric.

The epoxy resins, used in embodiments disclosed herein for component (a) of the present invention, may vary and include conventional and commercially available epoxy resins, which may be used alone or in combinations of two or more. In choosing epoxy

resins for compositions disclosed herein, consideration should not only be given to properties of the final product, but also to viscosity and other properties that may influence the processing of the resin composition.

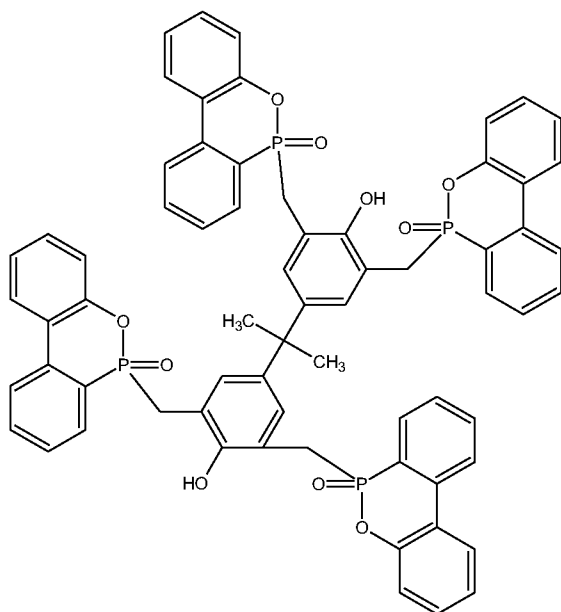
Examples of epoxy compounds include, but are not limited to epoxies based on reaction products of polyfunctional alcohols, phenols, cycloaliphatic carboxylic acids, aromatic amines, or aminophenols with epichlorohydrin. A few non-limiting embodiments include, for example, bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, resorcinol diglycidyl ether, and triglycidyl ethers of para-aminophenols. Other suitable epoxy resins known to the skilled worker include reaction products of epichlorohydrin with o-cresol and, respectively, phenol novolacs. Further epoxy resins include epoxides of divinylbenzene or divinylanthracene. It is also possible to use a mixture of two or more epoxy resins.

The epoxy resins useful in the present invention may be selected from commercially available products; for example, D.E.R®. 331, D.E.R. 332, D.E.R. 383, D.E.R. 334, D.E.N. 431, D.E.N. 438, D.E.R. 736, or D.E.R. 732 epoxy resins available from The Dow Chemical Company or Syna 21 cycloaliphatic epoxy resin from Synasia.

The curable composition may comprise 1 to 90 percent by weight of naphthol novolacs prepared by the method mentioned above (afterwards referred to as 'modified naphthol novolac' or 'm-NPN'). All individual values and subranges from 1 to 90 weight percent are included herein and disclosed herein, for example, the weight percent of m-NPN can be from a lower limit of 1, 1.2, 1.5, 12, or 20 weight percent to an upper limit of 45, 50, 54, 60, or 70 weight percent. For example, curable composition may comprise 1 to 60 percent by weight of one or more m-NPNs or in the alternative, curable composition may comprise 1 to 50 percent by weight of one or more m-NPNs.

The curable composition may comprise 1 to 80 percent by weight of one or more oligomeric compounds comprising a phosphorus composition which is the reaction product of an etherified resole with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). All individual values and subranges from 1 to 80 weight percent are included herein and disclosed herein, for example, the weight percent of DOPO compound can be from a lower limit of 1.5, 2, 3, 5, or 10 weight percent to an upper limit of 20, 40, 55, 60, or 70 weight percent. For example, curable composition may comprise 2 to 60 percent by weight of one or more DOPO compound or in the alternative, curable composition may comprise 5 to 40 percent by weight of one or more DOPO compound.

In an embodiment, the DOPO-containing compound is an oligomeric composition comprising a phosphorus-containing compound which is the reaction product of an etherified resole with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide ('H-DOP'). This reaction product, referred to hereinafter as 'DOP-BN,' is depicted in Formula I, below.



Formula I

Further information about DOP-BN and its preparation can be found in US Pat. No. 8,124,716.

In one or more embodiments, the curable composition can contain a solvent. Solvents can be used to solubilize the epoxy and hardener component or to adjust the viscosity of the final varnish. Examples of solvents that can be used include, but are not limited to methanol, acetone, n-butanol, methyl ethyl ketone (MEK), cyclohexanone, benzene, toluene, xylene, dimethylformamide (DMF), ethyl alcohol (EtOH), propylene glycol methyl ether (PM), propylene glycol methyl ether acetate (DOWANOLTM PMA) and mixtures thereof.

The curable composition can be produced by any suitable process known to those skilled in the art. In an embodiment, solutions of the epoxy component, phosphorus-containing compound, and polymeric anhydride are mixed together. Any other desired component, such as the optional components described above, are then added to the mixture.

Embodiments of the present disclosure provide preregs that includes a reinforcement component and the curable composition, as discussed herein. The prepreg can be obtained by a process that includes impregnating a matrix component into the reinforcement component.

The matrix component surrounds and/or supports the reinforcement component. The disclosed curable compositions can be used for the matrix component. The matrix component and the reinforcement component of the prepreg provide a synergism. This synergism provides that the prepregs and/or products obtained by curing the prepregs have mechanical and/or physical properties that are unattainable with only the individual components. The prepregs can be used to make electrical laminates for printed circuit boards.

The reinforcement component can be a fiber. Examples of fibers include, but are not limited to, glass, aramid, carbon, polyester, polyethylene, quartz, metal, ceramic, biomass, and combinations thereof. The fibers can be coated. An example of a fiber coating includes, but is not limited to, boron.

Examples of glass fibers include, but are not limited to, A-glass fibers, E-glass fibers, C-glass fibers, R-glass fibers, S-glass fibers, T-glass fibers, and combinations thereof. Aramids are organic polymers, examples of which include, but are not limited to, Kevlar®, Twaron®, and combinations thereof. Examples of carbon fibers include, but are not limited to, those fibers formed from polyacrylonitrile, pitch, rayon, cellulose, and combinations thereof. Examples of metal fibers include, but are not limited to, stainless steel, chromium, nickel, platinum, titanium, copper, aluminum, beryllium, tungsten, and combinations thereof. Examples of ceramic fibers include, but are not limited to, those fibers formed from aluminum oxide, silicon dioxide, zirconium dioxide, silicon nitride, silicon carbide, boron carbide, boron nitride, silicon boride, and combinations thereof. Examples of biomass fibers include, but are not limited to, those fibers formed from wood, non-wood, and combinations thereof.

The reinforcement component can be a fabric. The fabric can be formed from the fiber, as discussed herein. Examples of fabrics include, but are not limited to, stitched fabrics, woven fabrics, and combinations thereof. The fabric can be unidirectional, multiaxial, and combinations thereof. The reinforcement component can be a combination of the fiber and the fabric.

The prepreg is obtainable by impregnating the matrix component into the reinforcement component. Impregnating the matrix component into the reinforcement component may be accomplished by a variety of processes. The prepreg can be formed by contacting the reinforcement component and the matrix component via rolling, dipping, spraying, or other such procedures. After the prepreg reinforcement component has been contacted with the prepreg matrix component, the solvent can be removed via volatilization. While and/or after the solvent is volatilized the prepreg matrix component can be cured, e.g.

partially cured. This volatilization of the solvent and/or the partial curing can be referred to as B-staging. The B-staged product can be referred to as the prepreg.

For some applications, B-staging can occur via an exposure to a temperature of 60 °C to 250 °C; for example B-staging can occur via an exposure to a temperature from 65 °C to 240 °C, or 70 °C to 230 °C. For some applications, B-staging can occur for a period of time of 1 minute (min) to 60 min; for example B-staging can occur for a period of time from, 2 min to 50 min, or 5 min to 40 min. However, for some applications the B-staging can occur at another temperature and/or another period of time.

One or more of the prepregs may be cured (e.g. more fully cured) to obtain a cured product. The prepregs can be layered and/or formed into a shape before being cured further. For some applications (e.g. when an electrical laminate is being produced) layers of the prepreg can be alternated with layers of a conductive material. An example of the conductive material includes, but is not limited to, copper foil. The prepreg layers can then be exposed to conditions so that the matrix component becomes more fully cured.

One example of a process for obtaining the more fully cured product is pressing. One or more prepregs may be placed into a press where it subjected to a curing force for a predetermined curing time interval to obtain the more fully cured product. The press has a curing temperature in the curing temperature ranges stated above. For one or more embodiments, the press has a curing temperature that is ramped from a lower curing temperature to a higher curing temperature over a ramp time interval.

During the pressing, the one or more prepregs can be subjected to a curing force via the press. The curing force may have a value that is 10 kilopascals (kPa) to 350 kPa; for example the curing force may have a value that is 20 kPa to 300 kPa, or 30 kPa to 275 kPa. The predetermined curing time interval may have a value that is 5 s to 500 s; for example the predetermined curing time interval may have a value that is 25 s to 540 s, or 45 s to 520 s. For other processes for obtaining the cured product other curing temperatures, curing force values, and/or predetermined curing time intervals are possible. Additionally, the process may be repeated to further cure the prepreg and obtain the cured product.

The prepregs can be used to make composites, electrical laminates, and coatings. Printed circuit boards prepared from the electrical laminates can be used for a variety of applications. In an embodiment, the printed circuit boards are used in smartphones and tablets. In various embodiments, the electrical laminates have a copper peel strength in the range of from 4 lb/in to 12 lb/in.

EXAMPLES

Inventive Synthesis of Modified Naphthol Novolac (m-NPN)

1-Naphthol (24 grams, 0.17 mol) and 2-naphthol (12 grams, 0.083 mol) were dissolved in toluene (75 mL) at 50 °C (using a 250 ml 3-neck round bottom flask equipped with a stirrer, condenser and a tube for introduction of N₂). After the solids disappeared, oxalic acid (300 milligrams, 5 mmol) was added followed by paraformaldehyde (PF) (6.75 g, 0.225 mol). The reaction mixture was slowly heated to 90 °C. A large quantity of bubbles appeared along with the depolymerization of formaldehyde and the condensation reaction occurred with a violent reflux. After it was stabilized, the mixture was refluxed with stirring for 6.5 hours. It was cooled to 50 °C and the upper toluene solution was discarded. The residue was dissolved with cyclohexanone (30 ml) at 80 °C for 1 hour, after which the solution could be used without further purification. A small portion was taken out and dried at 80 °C in a vacuum oven for 3 hours. The weight loss of the sample was used to calculate the concentration of the naphthol novolac composition in cyclohexanone.

Comparative Synthesis of Naphthol Novolac (NPN)

To a 1000 mL three neck round-bottom-flask equipped with refluxing condenser, mechanical stirrer and temperature sensor, 72 grams of 1-naphthol (0.5 mol) was added to 200 mL toluene. The mixture was heated to 70°C to disperse 1-naphthol into the solvent. 13 grams of paraformaldehyde (0.5 * 0.87 mol) and 1.26 grams of oxalic acid (0.5 * 0.02 mol) were then added. The reaction mixture was then heated carefully to 110°C and stirred under N₂ atmosphere for 72 hours. The reaction mixture was allowed to cool to 50°C and the products precipitated from the solution. The upper toluene solution was discarded and 200 mL of ethyl acetate was added and the mixture was stirred for an additional 10 minutes. The ethyl acetate solution was washed with water once and then with a NaCl solution twice. The organic phase was collected and dried over anhydrous sodium sulfate for 2 hours. Then the salt was filtrated and most of the solvent was removed under vacuum. Finally, the product was dried in vacuum oven at 100°C overnight. The yield was 80%. The naphthol monomer content in the final product was 0.4%. ¹H NMR (acetone-d₆, 400 MHz): 8.31-6.96 ppm (m, 6H); 4.54-4.05 ppm (m, 1.5 H); GPC (THF): Mn: 1008g/mol; Mw: 1615g/mol; D: 1.60.

Characterization method

Table 1 - Gel Permeation Chromatography (GPC) Settings

Instrument	Agilent 1200
Columns	Two Mixed E columns (7.8x300mm) in tandem.
Column Temperature	40 °C
Mobile Phase	Tetrahydrofuran
Flow	1.0 mL/min
Injection volume	50 µL
Detector	Agilent Refractive Index detector, 40 °C
Software	Agilent GPC software. Data were collected from duplicate injections.
Calibration Curve	PL Polystyrene Narrow standards (Part No.:2010-0101) with molecular weights ranging from 19,760 to 162 g/mol, using polynom 3 fitness.

Table 2 shows the GPC results of naphthol novolac compositions prepared under different conditions. Comparative Example A was prepared using the Comparative Synthesis and Comparative Example B was prepared using the Inventive Synthesis. Examples 1-4 were all prepared using the Inventive Synthesis. The molecular weight of m-NPN could be controlled by the reaction time and the molar ratio of 1-naphthol and 2-naphthol. Since 2-naphthol tended to dimerize in the reaction with formaldehyde, increasing the ratio of 2-naphthol in the starting material resulted in the decrease of molecular weight of the product. Shortening the reaction time also resulted in a naphthol novolac composition having a lower molecular weight.

Table 2 - Results of Gel Permeation Chromatography for m-NPN

NPN/m-NPN	Reaction conditions				Mn (g/mol)	Mw (g/mol)	PDI
	1-Naphthol	2-Naphthol	PF	Reaction time			
Comparative Example A	1 mol	0	0.87 mol	48 h	1008	1615	1.60
Comparative Example B	1 mol	0	0.87 mol	48 h	1105	1848	1.67
Example 1	0.75 mol	0.25 mol	0.90 mol	24 h	1020	1379	1.35
Example 2	0.67 mol	0.33 mol	0.90 mol	6.5 h	778	1111	1.43
Example 3	0.50 mol	0.50 mol	0.80 mol	6.5 h	578	758	1.31
Example 4	0.33 mol	0.67 mol	0.75 mol	6.5 h	452	583	1.29

Thermal properties of Naphthol Novolac-Based Non-Halogen Formulations

Ingredients

DENTM ('DEN') 438 (XZ 92748): phenol novolac type epoxy, from The Dow Chemical Company;

- 5 DOP-BN (XZ 92741), hardener containing phosphorus, from The Dow Chemical Company;
Naphthol Novolac (NPN) or Modified Naphthol Novolac (m-NPN): formulations shown in Table 2, above.

2MI: curing catalyst (10% in methanol), from Sigma-Aldrich.

10

Table 3 - Formulation

	EEW or HEW	EEW/HEW	Solid Weight /g	Solid / mol	solid content	solution weight/g	P%
XZ 92748	178	110.00%	1.3597	0.0076	85%	1.5997	0.00%
NPN/m-NPN	152		0.7600	0.0050	60%	1.2667	
XZ 92741	450		0.8750	0.0019	57%	1.5351	8.90%
Total /g			2.9947			4.4014	2.60%
2-MI					10%	0.0165	

Sample preparation

- 15 The above ingredients were mixed according to the above formulation and shaken to
form a uniform solution. The catalyst was then added to the varnish, and gel time of the
varnish was tested on a hot plate maintained at 171°C. The gelled material was recovered
from the hot plate surface and post-cured in an oven at 200°C for 3 hours. The glass transition
temperature (T_g) of the cured material was measured by DSC.

- 20 The above varnish was brushed on an E-glass fiber sheet (Hexcel 7628) and the glass
fiber sheet was then put into a 177°C oven with good air flow for the given time to obtain the
prepregs. The prepregs were then crushed to collect powder.

A clear plaque was made for dielectric and DMTA measurement. Prepreg powder was placed on a flat aluminum foil, and then the aluminum foil with the powder was placed on a flat metal plate. The assembly was heated to 200 °C until the powder melted. The melted powder was covered with another aluminum foil and then a flat metal plate was placed on the aluminum foil. The assembly was hot pressed at 200 °C for 1 hour and then was post cured at 200 °C for another 3 hours. An air bubble-free plaque with a thickness of 0.3 mm was obtained and used for D_k/D_f and DMTA testing.

Test methods

10 Differential scanning calorimetry (DSC)

DSC experiments were carried out using a DSC-Q2000 instrument under a flowing nitrogen atmosphere (50 ml/min). About 10 mg cured resin was used in the examination. A dynamic temperature scan from 40°C to 280°C was applied at a heating rate of 10°C/min. Two scans were obtained using the same ramp rate.

15

Dynamic Mechanic Thermal Analysis (DMTA)

The glass transition temperature (T_g) of the laminate was also measured by dynamic mechanic thermal analysis (DMTA). The T_g was determined from the maximum in the tangent delta peak. The testing parameters are below:

20 Frequency: 6.28 rad/s

Initial Temp: 20.0 °C

Final Temp: 350.0°C

Ramp Rate = 3.0°C/min

25 Dielectric Constant/Dissipation Factor (D_k/D_f) Measurements

Samples were analyzed at room temperature by an Agilent 4991A Impedance/Material Analyzer equipped with Agilent 16453A test fixture. Calibration was done using an Agilent Teflon standard plaque using D_k/D_f parameters provided by vendor. Thickness of Teflon standard plaque and all samples was measured by micrometer.

Results in Table 4 show the thermal properties of the materials cured with m-NPN with different molecular weights (as described above, higher ratio of 1-N and 2-N means higher molecular weight). The relationship of glass transition temperature T_g and molecular weights of m-NPN was investigated using the non halogen formulation. XZ 92748 co-cured by DOP-BN and m-NPN with higher molecular weight exhibited higher T_g . For F4, when m-NPN prepared from 1-N and 2-N in a ratio of 3:1, the corresponding resin showed similar T_g (188 °C) with Comparative B (186 °C) which used high molecular weight NPN as the hardener. Compared with Dow's product phenol novolac (PN, XZ 92535) (Comparative A), T_g was improved by 20 °C when 1-naphthol was used as the major component in the starting material (the ratio of 1-N and 2-N is higher than 2:1) (F3, F4).

Table 4 - Thermal Properties of -Non-Halogen Formulations

Component	Comparative Ex C	Comparative Ex D	Example 5	Example 6	Example 7	Example 8
Epoxy	XZ 92748	XZ 92748	XZ 92748	XZ 92748	XZ 92748	XZ 92748
Hardener	PN (XZ92535)	Comp Ex A	Example 4	Example 3	Example 2	Example 1
Hardener	DOP-BN	DOP-BN	DOP-BN	DOP-BN	DOP-BN	DOP-BN
T_g (DSC/°C)	165	186	169	173	183	188

Formulations having different multifunctional epoxy resins were tested for thermal properties. The multifunctional epoxy resins were screened in small amounts (ca. total 3.0 g of varnish). DOP-BN was also added to the formulations to adjust the phosphorous content to a certain level for flame retardant (FR) properties. Owing to the lower molecular weight, when eCHTP (four functionality epoxy, 74.2% in methyl ethyl ketone, from The Dow Chemical Company) and XZ 97109 (Bisphenol A novolac type epoxy, 75% in methyl ethyl ketone, from The Dow Chemical Company) were used as the epoxy components, formulations containing the composition of Example 1 (Example 9 and Example 10) showed slightly lower T_g values than Comparative Examples E and F by 9°C and 7°C, respectively (Table 5). It was also demonstrated that eCHTP showed the highest thermal stability in these formulations compared with the other tested epoxy resins such as XZ 97109, Tactix 742 and M-BOND 450 (part A).

Table 5 - Thermal Results of NPN/m-NPN Cured Casts

Component	Comparative E	Example 9	Comparative F	Example 10	Example 11	Example 12
Epoxy	eCHTP	eCHTP	XZ 97109	XZ 97109	Tactix 742	M-BOND 450 (part A)
Hardener	Comp Ex A	Example 1	Comp Ex A	Example 1	Example 1	Example 1
Hardener	DOPO-BN	DOPO-BN	DOPO-BN	DOPO-BN	DOPO-BN	DOPO-BN
P wt % (in total solid)	2.6%	2.6%	2.6%	2.6%	2.6%	2.6%
Tg (DSC/°C)	245	236	221	214	213	
Tg (DMA/°C)						200

Properties of the laminates

Preparation of the laminates

- 5 A Laminate based on Example 10 was prepared. The detailed varnish formulation is listed in Table 6. The polymer ingredients were mixed to form a uniform 60% solution in cyclohexanone. The above mixture was shaken for 1 hour. The varnish was then painted on glass fiber sheets (Hexcel 7628) and partially cured at 171°C in a ventilated oven for a suitable time (generally, about 3 minutes) to make preregs. Finally, 8 pieces of preregs
- 10 were hot pressed at 200 °C for one hour to make a hand-painted laminate, the laminate was post cured at 200°C for another two hours.

Table 6 – Varnish Formulation for the Laminates

	EEWor HEW	EEW/HEW	Solid Weight /g	Solid / mol	solid content	solution weight/g	P%
XZ 97109	212	110.00%	52.97	0.2498	75%	70.62	0.00%
m-NPN (Ex 1)	152		19.60	0.1832	50%	39.20	
XZ 92741	450		30.00	0.06667	57%	52.63	8.90%
Cyclohexano ne						8.50	
Total /g			86.16			170.95	2.60%
2-MI					10%	0.30	

Properties of the hand-painted laminates

- 15 The properties of the laminates were tested and detailed results are shown in Table 7. Compared with a phenol novolac (XZ 92535, phenol novolac, 50% in PMA, from Dow Chemical Company) -based laminate (same formulation in Table 6, using PN to replace NPN), the NPN-based non-halogen formulation shows higher Tg (204 °C by DSC) and Td, and lower moisture uptake. At 2.6% phosphorous content (based on total solids), both of
- 20 laminates could pass the UL94 test with a V-0 rating. The total burn time for the NPN based

laminate was 34 seconds, which was shorter than the PN-based counterpart (borderline, 49 seconds). It also showed promising mechanical properties, as well as low Z-axis coefficient of thermal expansion and dielectrical properties (Dk and Df).

Table 7 – Performance of Hand-Painted Laminates

Sample	thickness of the laminate (8 layer board)	T _g by DSC (°C)	T _d (°C) (5% WTL, TGA)	α_1 (ppm/°C) (Z-axis CTE, TMA)	Delamination time (T288, min)	Dk/Df@ 1GHz	Moisture uptake	UL94 V-0	Copper peel strength
PN based laminate	1.65 mm	193	354	59.27/3.3	> 60 min	4.25/0.015	0.35%	pass	8.0
m-NPN based laminate	1.68 mm	204	370	60.26/3.0	> 60 min	4.44/0.015	0.25%	pass	N/A

CLAIMS

1. A method for making naphthol novolac comprising:
contacting
 - 5 a) a naphthol component comprising
 - i) from 1 to 99 weight percent 1-naphthol; and
 - ii) from 1 to 99 weight percent 2-naphthol; and
 - b) an aldehydein a reaction zone under reaction conditions to form the naphthol novolac.
- 10 2. A method in accordance with claim 1 wherein the reaction conditions comprise a reaction temperature of from 80°C to 160°C and a reaction time of 3 to 72 hours.
3. A method in accordance with any of the preceding claims wherein the aldehyde is paraformaldehyde.
- 15 4. A method in accordance with any of the preceding claims wherein the naphthol component is present in a solvent prior to the contacting with the aldehyde.
5. A curable composition comprising:
 - a) an epoxy resin; and
 - b) a hardener component comprising
 - 20 i) an oligomeric compound comprising a phosphorus composition which is the reaction product of an etherified resole with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, and
 - ii) a naphthol novolac prepared by the method of claim 1.
6. A curable composition in accordance with claim 5 further comprising a filler selected
25 from the group consisting of natural silica, fused silica, alumina, hydrated alumina, and combinations thereof.
7. A curable composition in accordance with any one of claims 5 or 6 wherein the epoxy resin is selected from the group consisting of phenol novolac epoxy, diglycidyl ether of bisphenol A and combinations thereof.
- 30 8. A curable composition in accordance with any one of claims 5-7 wherein the phosphorus-containing compound is DOP-BN.
9. A curable composition in accordance with any one of claims 5-8 further comprising a catalyst.

10. A curable composition in accordance with any one of claims 5-9 wherein the epoxy component is present in an amount in the range of from 10 weight percent to 90 weight percent, the phosphorus-containing compound is present in an amount in the range of from 2 weight percent to 60 weight percent, and the naphthol novolac is present in an amount in the range of 1 weight percent to 60 weight percent, based on the total weight of the formulation.
11. A curable composition in accordance with any one of claims 6-10 wherein the filler is present in an amount in the range of from 10 weight percent to 80 weight percent.
12. A curable composition in accordance with any one of claims 9-11 wherein the catalyst is present in an amount in the range of from 0.01 weight percent to 50 weight percent.
13. A process for preparing the curable composition of any one of claims 5-12 comprising admixing a) an epoxy resin; and b) a hardener component comprising i) an oligomeric compound comprising a phosphorus composition which is the reaction product of an etherified resole with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, and ii) the naphthol novolac to form the curable composition.
14. A prepreg prepared from the curable composition of any one of claims 5-12.
15. An electrical laminate prepared from the curable composition of any one of claims 5-12.
16. A printed circuit board prepared from the electrical laminate of claim 15.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2014/085579

A. CLASSIFICATION OF SUBJECT MATTER

C08G 8/08(2006.01)i; C08L 61/08(2006.01)i; C07F 9/547(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G; C08L; C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, CNPAT, EPODOC, CNKI, CA, ISI Web of Knowledge:alpha-naphthol, aldehyd+, novolac, resin+, epoxy, beta-naphthol+, alpha-naphthol+, naphtho+, 1-naphthol, hydroxynaphthalene, DOP, phosphorus, CAS RN: 90-15-3, 135-19-3

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5302673 A (DAI ICHI KOGYO SEIYAKU CO LTD ET AL.) 12 April 1994 (1994-04-12) abstract, example 1; column 3, line 6 to column 4, line 17	1-4
Y	US 5302673 A (DAI ICHI KOGYO SEIYAKU CO LTD ET AL.) 12 April 1994 (1994-04-12) abstract, example 1; column 3, line 6 to column 5, line 21; column 7, lines 13-26	5-16
Y	US 2011054077 A1 (DOW GLOBAL TECHNOLOGIES INC) 03 March 2011 (2011-03-03) paragraphs [0028], [0136], [0202]-[0203], [0231]	5-16
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X	JP 0680761 A (DAI ICHI KOGYO SEIYAKU CO LTD) 22 March 1994 (1994-03-22) examples 1-5	1-4
A	JP 2013067697 A (DAINIPPON INK & CHEMICALS) 18 April 2013 (2013-04-18) abstract, example 1	1-16

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

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“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2014/085579

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