

OLIGOMERIC HALOGENATED CHAIN EXTENDERS FOR PREPARING EPOXY RESINS

The present invention relates to a process for making oligomeric
5 halogenated chain extender compositions and reaction products of such chain
extenders, which in turn can be used for making thermally resistant epoxy resin
compositions. The thermally resistant epoxy resins, are useful, for example, in
electrical laminate applications, such as for the manufacture of printed wiring boards.

There are several commonly used indicators of thermal performance of
10 electrical laminates. One of these is the glass transition temperature (T_g) of the cured
resin. Another measure is the thermal decomposition temperature (T_d) of the cured
resin, which is determined using thermogravimetric analysis (TGA). A third indicator
is known as "T260", which is the time required for a laminate to begin to decompose
when heated to 260°C. A similar indicator is "T288", which measures the
15 decomposition time at 288°C. A fourth, but related, indicator is solder dip resistance,
which is the time required for the laminate to begin to delaminate when it is dipped
into molten solder at 288°C.

Recently, industry standards have begun to specify that lead-free
solders be used to construct electronic devices. The lead-free solders usually melt at
20 higher temperatures than conventional lead-based solders. The use of these solders
therefore places greater demands on the thermal stability of the resin phase of the
electrical laminate. Conventional resins have not been able to satisfy these added
thermal requirements.

Another circumstance that drives the need for better thermal stability is
25 the production of multilayer boards. These are formed by bonding thin pre-processed
boards together using prepreg layers. This operation can be repeated several times.
With each repetition, the entire board is subjected to a complete thermal cure cycle.
As a result, the higher the layer count, the greater is the thermal impact on the inner
layer board.

30 Therefore, it is desirable to provide a resin that can enable the laminate
to exhibit the needed thermal properties. Laminates exhibiting a T_d of 310°C or
higher are expected to become standard in the industry. The T260 value should be at
least 15 minutes, and preferably at least 30 minutes, but values of an hour or more

are especially desired. T₂₈₈ values in excess of 5 minutes are also desired. The T_g should be 130°C or more, and preferably at least 150°C.

These thermal properties cannot be achieved at the expense of other desirable attributes of the resin and the laminate. The resin must be easily processed,
5 must have acceptable flow characteristics during the lamination step, and must have the necessary physical properties characteristics need to produce dimensionally stable laminates.

Epoxy resins are widely used to make electrical laminates. The resins are often brominated in order to impart the needed thermal properties to them. An
10 example of such a brominated epoxy resin composition is described in U. S. Patent No. 5,405,931 to Kohno et al. In the process described in that patent, an oligomer having terminal phenolic groups is prepared by reacting an excess of a halogenated phenolic compound with a glycidyl ether of a halogenated phenolic compound. The oligomerization reaction is performed in a melt of the starting materials. This
15 oligomer is advanced with another epoxy resin and then cured to form the polymer phase of an electrical laminate.

This invention is a process comprising forming a reaction mixture containing at least one epoxide-reactive compound and at least one halogenated epoxy resin in the presence of a solvent, and subjecting the reaction mixture to conditions
20 sufficient to form a solution of an oligomer composition in the solvent, wherein the oligomer composition contains terminal epoxide-reactive groups.

This invention is also a process comprising forming a mixture of (1) a solution of a halogenated oligomer composition having terminal epoxide-reactive groups and (2) and epoxy resin, and subjecting the mixture to conditions sufficient to
25 form an advanced, halogenated epoxy resin. This invention is also a process which further comprises curing the advanced, halogenated epoxy resin by reacting it with at least one epoxy curing agent.

This invention is also a solution of a halogenated oligomer composition in a solvent, wherein the oligomer composition has terminal epoxide-reactive groups.
30 The invention also includes a varnish that includes a solvent, the halogenated oligomer composition, at least one epoxy resin and at least one epoxy curing agent.

The invention is in other respects an advanced, halogenated epoxy resin formed by reacting the oligomer composition with an excess of at least one epoxy resin,

and a cured epoxy resin formed by reacting the advanced, halogenated epoxy resin with at least one epoxy curing agent.

This invention is also a varnish prepared from the advanced, halogenated epoxy resin. The varnish may contain, in addition to the advanced, halogenated epoxy resin, at least one epoxy curing agent, at least one additional epoxy resin, an inhibitor such as boric acid. The invention is in a further aspect a prepreg having a resin phase that includes the advanced, halogenated epoxy resin, optionally in combination with at least one other epoxy resin. The invention is still further a resin-coated foil or an electrical laminate having a resin phase produced by curing the advanced, halogenated epoxy resin (optionally in combination with at least one other epoxy resin), or mixture of the halogenated oligomer and at least one epoxy resin, with at least one epoxy curing agent.

It has been found that the process of forming the oligomer composition of the invention can have a very significant impact upon the thermal properties of a cured epoxy resin made using the oligomer composition. Using the process of the invention, cured epoxy resins having particularly good thermal properties can be formed. In particular, electrical laminates having T260 values in excess of 15 minutes and in some cases over an hour have been prepared in accordance with the invention. T_d values of greater than 300°C have been obtained. The cured epoxy resin retains other desirable attributes, including good physical properties (in particular, good toughness together with high T_g), good flow control and good adhesion.

The oligomer composition of the invention is produced by reacting at least one epoxide-reactive compound with a halogenated epoxy resin in the presence of a solvent. The epoxide-reactive compound may be halogenated or non-halogenated. A mixture of one or more non-halogenated epoxide-reactive compounds with one or more halogenated epoxide-reactive compounds can be used. Similarly, one or more non-halogenated epoxy resins can be used in combination with the halogenated epoxy resin. The oligomer composition is produced in the form of a miscible mixture in the solvent.

The oligomer composition contains terminal epoxide-reactive groups. In addition, the oligomer composition may also contain residual epoxide groups. If the oligomer composition contains residual epoxide groups, the ratio of equivalents of epoxide-reactive groups to equivalents of residual epoxide groups should be at least

1:1. This ratio is preferably is at least 2:1. This ratio can be any greater value, theoretically approaching infinity as the number of epoxide groups approaches zero. A practical upper limit on this ratio is 100:1. A more typical range for this ratio is from 2:1 to 30:1. When the ratio is within the low end of this range, such as from 2:1 to 8:1, 5 T_g tends to be somewhat higher in laminates made from the oligomer composition, although T_d , T_{260} and T_{288} values may be slightly lower.

The epoxide-reactive compound(s) are used in a stoichiometric excess over the epoxy resin to make the oligomer composition. The molar ratios of starting materials are selected such that the oligomer composition has a number average 10 molecular weight of from 600 to 4000, and a weight average molecular weight of from 1200 to 10,000. A preferred number average molecular weight is from 700 to 3200 and a preferred weight average molecular weight is from 1500 to 7000. An especially preferred number average molecular weight is from 800 to 1600 and an especially preferred weight average molecular weight is from 1500 to 3500. These molecular 15 weight values include the contribution of any unreacted epoxide-reactive compounds as may be present in the oligomer composition.

Hydroxyl equivalent weights are suitably from 300 to 2000, preferably from 500 to 1000. Epoxide equivalent weights are generally higher, typically being at least 1200 and preferably being from 1400 to 10,000.

20 The oligomer composition will typically comprise a mixture of compounds having varying degrees of polymerization. Usually, it will also contain a quantity of unreacted starting materials, mainly the epoxide-reactive compound(s), as they are used in excess. Unreacted epoxy compounds will be present in very small quantities, if at all, although some epoxy-functional species may be present as 25 discussed above. In cases in which the oligomer composition is made from difunctional starting materials (as is preferred), the epoxide-reactive compounds(s) are used in significant excess (at least two times the number of equivalents of epoxide groups) and the reaction is continued until most of the epoxide groups in the starting materials are consumed, the bulk of the weight of the oligomer will consist of molecules containing N 30 repeating units derived from the epoxide-reactive compound and N-1 repeating units derived from the epoxy resin. N can range from 2 to 50, but preferably is mainly 2 to 10 and most preferably will be mainly from 2-5. Preferred oligomer compositions are those in which the molecules corresponding to N values of 2 or 3 constitute at least 48

percent of the weight of the oligomer (based on solids, exclusive of any solvent that may be present. Molecules corresponding to N values of 2 or 3 preferably constitute from 48 to 75 percent by weight of the oligomer. The oligomer composition may contain up to 30 percent by weight of unreacted epoxide-reactive starting compounds,
 5 again on a solids basis.

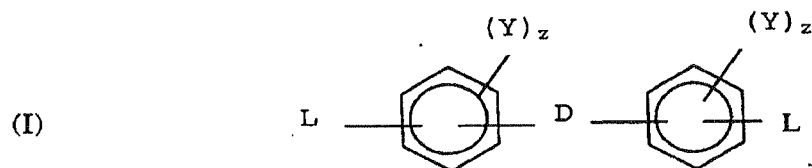
When the epoxide-reactive compound is used in lesser amounts, or when the reaction is not continued as long, the oligomer will tend to contain a broader range of species, including unreacted epoxide-reactive compound, a small amount of unreacted halogenated epoxy resin, and a range of oligomerized reaction products.
 10 The oligomerized reaction products will generally include molecules having no epoxy groups, molecules having no epoxide-reactive groups, and molecules of varying degrees of polymerization that have both epoxy and epoxide-reactive groups.

The oligomer composition may contain from 10 to 60 percent by weight, especially from 25 to 55 percent by weight, and especially from 35 to 55 percent by
 15 weight of halogen atoms. The halogen atoms are preferably chlorine and more preferably bromine. Mixtures of chlorine and bromine can also be used.

A suitable halogenated epoxide-reactive compound for making the oligomer contains at least one halogen atom and at least 2 epoxide-reactive groups/molecule. The halogen atoms are preferably chlorine and/or bromine and are
 20 most preferably bromine. The compound preferably contains exactly 2 epoxide-reactive groups per molecule.

Epoxide-reactive groups are functional groups that will react with a vicinal epoxide to form a covalent bond. These groups include phenol, isocyanate, carboxylic acid, amino or carbonate groups, although amino groups are less preferred.
 25 Phenols are preferred. A phenolic hydroxyl group is any hydroxyl group that is attached directly to an aromatic ring carbon atom.

Suitable halogenated epoxide-reactive compounds include those represented by the structure (I)



where each L independently represents an epoxide-reactive group, Y represents a halogen atom, each z is independently a number from 1 to 4 and D is a divalent hydrocarbon group suitably having from 1 to 10, preferably from 1 to 5, more preferably from 1 to 3 carbon atoms, -S-, -S-S-, -SO-, -SO₂-, -CO₃-, -CO- or -O-. The preferred halogenated epoxide-reactive compounds are halogenated phenolic compounds in which each L is -OH. Examples of the halogenated phenolic compound include mono-, di-, tri- and tetrachloro-substituted and mono-, di-, tri- and tetrabromo-substituted dihydric phenols such as bisphenol A, bisphenol K, bisphenol F, bisphenol S and bisphenol AD, and mixtures thereof. Tetrabromo-substituted bisphenols are particularly preferred.

Suitable nonhalogenated epoxide-reactive compounds that are useful to make the oligomer preferably corresponds to structure (I), except each z is zero in this case. Examples include dihydric phenols such as bisphenol A, bisphenol K, bisphenol F, bisphenol S and bisphenol AD, and mixtures thereof.

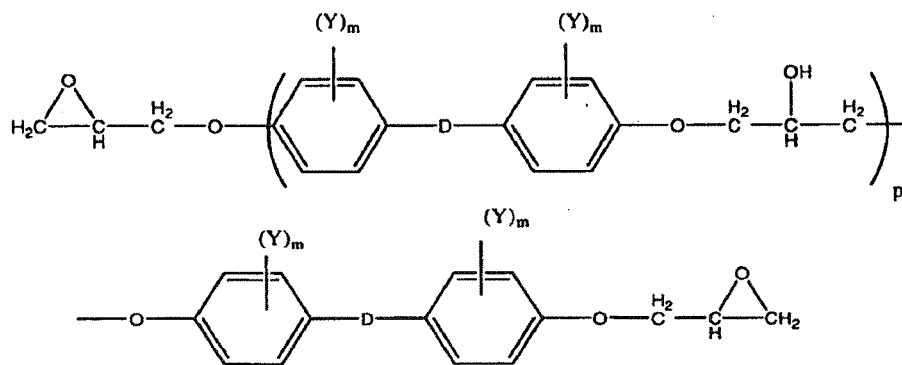
Epoxide-reactive compounds (either halogenated or non-halogenated) having three or more phenolic groups, such as tetraphenol ethane, may also be used to make the oligomer, although they will usually be used in small quantities such as no greater than 5 percent of the total weight of the epoxide-reactive compounds.

The epoxide-reactive compound(s) (whether halogenated or not) preferably contain less than 2 percent, especially less than 1 percent, by weight of nitrogen. They are most preferably devoid of nitrogen.

The halogenated epoxy resin used to make the oligomer composition contains at least one halogen atom and two or more, preferably exactly two, epoxide groups per molecule. As before, the halogen atoms are preferably chlorine and/or bromine and most preferably are bromine. The halogen atoms are preferably bonded to a carbon atom of an aromatic ring.

The halogenated epoxy resin used to make the oligomer composition may be a saturated or unsaturated aliphatic, cycloaliphatic, aromatic or heterocyclic compound. It can be substituted with one or more substituents such as lower alkyl. The halogenated epoxy resin may have an epoxy equivalent weight of 150 to 3,500, preferably 160 to 1000, more preferably from 170 to 500. Suitable halogenated epoxy resins are well described in, for example, U.S. Patent Nos. 4,251,594, 4,661,568, 4,710,429, 4,713,137, and 4,868,059, and *The Handbook of Epoxy Resins* by H. Lee and K. Neville, published in 1967 by McGraw-Hill, New York.

A preferred type of halogenated epoxy resin is a diglycidyl ether of a polyhydric phenol. Suitable epoxy resins include those represented by the structure (II)



5 (II)

wherein each Y is independently a halogen atom, each D is a divalent group as described with respect to structure (I), m may be 1, 2, 3 or 4 and p is a number from 0 to 5, especially from 0 to 2. Examples of the halogenated epoxy resins include mono-, di-, tri- and tetrachloro-substituted and mono-, di-, tri- and tetrabromo-substituted diglycidyl ethers of dihydric phenols such as bisphenol A, bisphenol K, bisphenol F, bisphenol S and bisphenol AD, and mixtures thereof. Tetrabromo-substituted epoxy resins are particularly preferred. Diglycidyl ethers of tetrabromobisphenol A and derivatives thereof are commercially available from The Dow Chemical Company under the trademark names D.E.R.® 542 and D.E.R.® 560.

Mixtures of halogenated and non-halogenated epoxy resins can be used to make the oligomer. Suitable non-halogenated epoxy resins include, for example, the diglycidyl ethers of polyhydric phenol compounds such as resorcinol, catechol, hydroquinone, bisphenol, bisphenol A, bisphenol AP (1,1-bis(4-hydroxylphenyl)-1-phenyl ethane), bisphenol F, bisphenol K, tetramethylbiphenol, diglycidyl ethers of aliphatic glycols and polyether glycols such as the diglycidyl ethers of C₂₋₂₄ alkylene glycols and poly(ethylene oxide) or poly(propylene oxide) glycols; polyglycidyl ethers of phenol-formaldehyde novolac resins, alkyl substituted phenol-formaldehyde resins (epoxy novolac resins), phenol-hydroxybenzaldehyde resins, cresol-hydroxybenzaldehyde resins, dicyclopentadiene-phenol resins and dicyclopentadiene-substituted phenol resins, and any combination thereof.

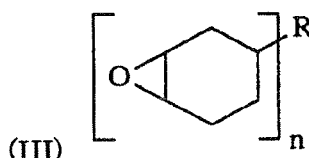
Suitable diglycidyl ethers of polyhydric phenolic compounds correspond to those represented by structure II above, in which m is zero. Many are commercially

available, including diglycidyl ethers of bisphenol A resins such as are sold by The Dow Chemical Company under the designations D.E.R.® 330, D.E.R.® 331, D.E.R.® 332, D.E.R.® 383, D.E.R.® 661 and D.E.R.® 662 resins.

Commercially available diglycidyl ethers of polyglycols that are useful as the non-halogenated epoxy resin include those sold as D.E.R.® 732 and D.E.R.® 736 by The Dow Chemical Company.

Epoxy novolac resins can be used as the nonhalogenated epoxy resin, but tend to be less preferred because they have epoxide functionalities in excess of 2.0. Such resins are available commercially as D.E.N.® 354, D.E.N.® 431, D.E.N.® 438 and D.E.N.® 439 from The Dow Chemical Company.

Other suitable additional epoxy resins are cycloaliphatic epoxides. A cycloaliphatic epoxide includes a saturated carbon ring having an epoxy oxygen bonded to two vicinal atoms in the carbon ring, as illustrated by the following structure III:



wherein R is an aliphatic, cycloaliphatic and/or aromatic group and n is a number from 1 to 10, preferably from 2 to 4. When n is 1, the cycloaliphatic epoxide is a monoepoxide. Di- or polyepoxides are formed when n is 2 or more. Mixtures of mono-, di- and/or polyepoxides can be used. Cycloaliphatic epoxy resins as described in U.S. Patent No. 3,686,359, may be used in the present invention. Cycloaliphatic epoxy resins of particular interest are (3,4-epoxycyclohexyl-methyl)-3,4-epoxy-cyclohexane carboxylate, bis-(3,4-epoxycyclohexyl) adipate, vinylcyclohexene monoxide and mixtures thereof.

Other suitable epoxy resins include oxazolidone-containing compounds as described in U. S. Patent No. 5,112,932. In addition, an advanced epoxy-isocyanate copolymer such as that sold commercially as D.E.R.® 592 and D.E.R.® 6508 (The Dow Chemical Company) can be used.

The non-halogenated resin preferably corresponds to structure II in which each m is zero. Examples of the nonhalogenated epoxy resins include diglycidyl ethers of dihydric phenols such as bisphenol A, bisphenol K, bisphenol F, bisphenol S and bisphenol AD, and mixtures thereof.

The halogenated epoxy resin and the additional epoxy resin, when used, are preferably mainly difunctional. If higher-functionality epoxy resins (whether halogenated or not) are used to make the oligomer, they are preferably used in small quantities, such as to 5 percent by weight of total weight of the epoxy resins used in making the oligomer composition.

The epoxide-reactive compound(s) and epoxy resin(s) are reacted in the presence of a solvent. The solvent is a material in which the reactants and the oligomer composition are soluble, at the temperature of the oligomerization reaction. The solvent is not reactive with the epoxide-reactive compound(s) or the epoxy resin(s) used to make the oligomer composition, under the conditions of the oligomerization reaction. The solvent (or mixture of solvents, if a mixture is used) preferably has a boiling temperature that is at least equal to and preferably higher than the temperatures employed to conduct the oligomerization reaction. A boiling temperature of from 100 to 150°C is especially suitable. Suitable solvents include, for example, glycol ethers such as ethylene glycol methyl ether and propylene glycol monomethyl ether; glycol ether esters such as ethylene glycol monomethyl ether acetate and propylene glycol monomethyl ether acetate; polyethylene oxide ethers and polypropyleneoxide ethers; polyethylene oxide ether esters and polypropylene oxide ether esters; amides such as N,N-dimethylformamide; aromatic hydrocarbons toluene and xylene; aliphatic hydrocarbons; cyclic ethers; halogenated hydrocarbons; and mixtures thereof. Preferred solvents include propylene glycol monomethyl ether, which are commercially available from The Dow Chemical Company as DOWANOL® PMA and DOWANOL® PM, respectively. These, can be used alone or in combination with another solvent, such as methyl ethyl ketone.

The solvent is present in an amount such that it constitutes at least 5 percent by combined weight of the solvent and starting materials (that is, epoxide-reactive compound(s) and epoxy resin(s)). Preferably, the solvent constitutes from 10 to 75 percent of the weight of the mixture, and more preferably constitutes from 15 to 60 percent of the weight of the mixture.

The oligomer composition is formed by bringing the mixture of solvent, the starting epoxide-reactive compound(s) and the starting epoxy resin(s) to a temperature above their respective melting temperatures, and permitting them to react until the epoxy groups on the epoxy resins are consumed. The starting materials can be mixed in any order provided that the solvent is present when

reaction conditions are achieved. The reaction can be conducted at a temperature of 100° to 200°C, preferably 110° to 180°C, for a period of 0.3 to 4 hours, preferably 1 to 3 hours.

The progress of the reaction can be followed by monitoring for epoxy content. The reaction should be continued until the epoxy content of the reaction mixture is reduced by at least half, and may be continued until the epoxy content is reduced to below measurable quantities. If the reaction proceeds until the epoxide content is reduced below 0.3 percent (based on weight of reactive starting materials), the resulting oligomer composition will contain a high ratio of epoxide-reactive groups to epoxy groups. If the epoxide content is reduced to 0.3 to 3.0 percent, the ratio of epoxide-reactive groups to epoxy groups will be lower. This often has the effect of increasing T_g in laminates made from the oligomer composition and in reducing reaction time in making the oligomer.

The oligomerization is preferably conducted in the presence of one or more catalysts for the reaction of epoxide groups with phenolic groups. Suitable such catalysts are described in, for example, U.S. Patent. Nos. 3,306,872, 3,341,580, 3,379,684, 3,477,990, 3,547,881, 3,637,590, 3,843,605, 3,948,855, 3,956,237, 4,048,141, 4,093,650, 4,131,633, 4,132,706, 4,171,420, 4,177,216, 4,302,574, 4,320,222, 4,358,578, 4,366,295, and 4,389,520. Examples of suitable catalysts are imidazoles such as 2-methylimidazole; 2-ethyl-4-methylimidazole; 2-phenyl imidazole tertiary amines such as triethylamine, tripropylamine and tributylamine; phosphonium salts such as ethyltriphenylphosphonium chloride, ethyltriphenylphosphonium bromide and ethyltriphenyl-phosphonium acetate; ammonium salts such as benzyltrimethylammonium chloride and benzyltrimethylammonium hydroxide; and mixtures thereof. The amount of the catalyst used generally ranges from 0.001 to 2 weight percent, and preferably from 0.01 to 1 weight percent, based on the total weight of the epoxide-reactive compounds and epoxy resins used to make the oligomer.

The oligomer composition prepared in this manner surprisingly exhibits excellent solubility in organic solvents such as propylene glycol monomethyl ether acetate and propylene glycol monomethyl ether. Similar oligomer compositions which are made in a fusion reaction process as described in US 5,405,931 tend to form turbid solutions which often phase separate upon standing, indicating that the oligomeric composition contains some insoluble fraction.

The halogenated oligomeric composition is useful as a chain extender or crosslinker for advancing epoxy resins. It can also be used as a reactive or non-reactive additive such as a flame retardant in thermoplastics.

To make a highly thermally resistant halogenated epoxy resin
5 composition useful for preparing electrical laminates, the oligomer composition is reacted with at least one additional epoxy resin to form an advanced resin, which can then be cured with one or more epoxy curing agents.

The additional epoxy resin has an average of more than one epoxy group per molecule. It preferably contains two or more epoxy groups/molecules, and more
10 preferably contains more than 2 epoxy groups/molecule.

The additional epoxy resin may be the same epoxy resin that is used to make the oligomeric composition, or may be a different resin. Higher functionality epoxy resins can be tolerated during the advancement step. It is preferably not halogenated, as the presence of halogen atoms in the additional epoxy resin can cause
15 undesired reactions with the epoxy curing agent and/or catalysts. The additional epoxy resin(s) may have an average epoxide functionality of 2 or greater, preferably at least 2.5 and more preferably at least 3. The use of a higher functionality epoxy resin in this step leads to a cured resin having a higher crosslink density, which tends to lead to better thermal properties. Suitable epoxy resins include glycidyl ethers of
20 phenolic compounds such as resorcinol, catechol, hydroquinone, bisphenol, bisphenol A, bisphenol AP (1,1-bis(4-hydroxyphenyl)-1-phenyl ethane), bisphenol F and bisphenol K. Preferred additional epoxy resins having an average of greater than 2 epoxy groups/molecule include cresol-formaldehyde novolac epoxy resins, phenol-formaldehyde novolac epoxy resins, bisphenol A novolac epoxy resins,
25 tris(glycidyloxyphenyl)methane, tetrakis(glycidyloxyphenyl)ethane, tetraglycidyl diaminodiphenylmethane and mixtures thereof. Tris(glycidyloxyphenyl)methane, tetrakis(glycidyloxyphenyl)ethane and tetraglycidyl diaminodiphenylmethane are preferred when a low viscosity resin is desired. In view of cost performance, cresol-formaldehyde novolac epoxy resins, phenol-formaldehyde novolac epoxy resins and
30 bisphenol A novolac epoxy resins or a mixture of these epoxy resins are of interest as the additional epoxy resin.

Epoxy novolac resins are of particular interest as the additional epoxy resin. These resins suitably have an epoxy equivalent weight of from 150 to 250,

especially from 160 to 210. Such resins are available commercially as D.E.N® 354, D.E.N® 431, D.E.N® 438 and D.E.N® 439 from The Dow Chemical Company.

The ratios of the halogenated oligomer composition and the additional epoxy resin are selected such that an epoxy-terminated advanced resin is formed
5 having a desired epoxy equivalent weight and a desired halogen content. A stoichiometric excess of the additional epoxy resin is needed in order to obtain an epoxy-terminated material. The epoxy equivalent weight of the advanced resin may be from 150 to 10,000 or more, preferably from 150 to 2000 and especially from 150 to 400. The halogen content of the advanced resin is suitably from 10 to 35, preferably
10 from 12 to 23, most preferably from 14 to 18 weight percent.

The advanced resin is conveniently prepared by heating a mixture of the oligomer composition and additional epoxy resin in the presence of a suitable catalyst. It is not necessary to remove the solvent from the halogenated oligomer before
15 conducting the advancement reaction, and in fact it is preferred that this solvent remains present. Additional solvents may be present if desired, although volatile materials that will evaporate at the reaction temperature are preferably avoided. The reaction is continued until the desired epoxy equivalent weight is obtained. The advanced material may include a mixture of unreacted additional epoxy resin and the halogenated oligomer composition/additional epoxy resin reaction product.

20 Suitable reaction conditions are generally the same as described for the preparation of the oligomer composition.

The resulting advanced epoxy resin is suitable in a variety of epoxy resin applications, either by itself or as a blend with one or more other epoxy resins. An application of particular interest is the preparation of electrical laminates. For
25 that application, a varnish is typically prepared by diluting the advanced epoxy resin in a suitable solvent. The varnish will also contain at least one epoxy curing agent and at least one catalyst for the curing reaction.

The particular curing agent used is not particularly critical and therefore a wide variety of curing agents can be used. However, the selection of curing
30 agent may affect thermal properties of the cured resin. These include amine curing agents such as dicyandiamide, diaminodiphenylmethane and diaminodiphenylsulfone; anhydrides such as hexahydroxyphthalic anhydride, copolymers of styrene-maleic acid anhydride; phenolic curing agents such as phenol novolac, bisphenol A novolacs; and mixtures thereof. Other curing agents useful in the present invention are

described in U.S. Published Patent Application No. 2004/0101689. The amount of the curing agents used will normally range from 0.3 to 1.5, especially from 0.8 to 1.2, equivalent per epoxy equivalent of the epoxy component(s) in the advanced resin.

Similarly, a wide range of catalysts can be used in the varnish
5 composition, including those described before with respect to the preparation of the oligomer. Suitable catalyst amounts are as described before, as well.

The varnish will include a solvent or a mixture of solvents. The solvent used for the epoxy resin composition may be the same material as that used to prepare the oligomer composition, as described above, or may be a different material. In
10 particular, lower-boiling solvents may be used in the varnish, as the solvent usually will be removed during the curing process.

The varnish may also contain an inhibitor to help control reactivity and in some cases to further increase the glass transition temperature of the cured system. Suitable such inhibitors include Lewis acids such as boric acid, boron oxide and boron
15 esters, as described in U. S. Patent No. 5,314,720 and 6,613,639.

The varnish may also include other additives such as pigments, dyes, fillers, surfactants, flow modifiers, flame retardants and mixtures thereof.

Alternatively, a varnish can be prepared in similar manner, using a mixture of the halogenated epoxide-reactive oligomer and an epoxy resin instead of (or
20 in addition to) the halogenated, advanced epoxy resin. Such a varnish fill also contain at least one epoxy curing agent as described before, and may contain other additives (such as catalysts) as discussed before.

To produce an electrical laminate, the varnish is impregnated into a substrate or web. The obtained impregnated substrate is dried at, for example, 80°C to
25 200°C, and preferably 100°C to 200°C; for 0.5 minute to 60 minutes, and preferably 0.5 minute to 30 minutes, to remove solvents and form a prepreg. Drying conditions are selected to minimize curing of the resin. The substrates used herein include, for example, glass cloth, a glass fiber, glass paper, carbon fiber, carbon fiber matts, paper, and similar substrates of aramid, polyamide, polyimide, polyester, and other
30 thermally stable polymeric fibers.

The obtained prepreg is cut into a desired size. Multiple sections of the cut prepreps (for example, 2 to 10 pieces) are stacked and laminated by application of

pressure and elevated temperature, such as, for example, 10 to 50 Kg/cm², and 130°C to 220°C, for 0.5 to 3 hours to cure the resin and obtain a laminate. An electrical conductive layer is formed on the laminate with an electrical conductive material. Suitable electrical conductive materials used herein include, for example, electrical
5 conductive metals such as copper, gold, silver, platinum and aluminum.

The electrical laminates manufactured as described above can be used as metal-clad laminates and multi-layer printed circuit boards for electrical or electronic equipment.

The use of a halogenated oligomer prepared in the solvent has been
10 found to lead to improvements in the thermal properties of the cured resin and the resulting laminate. Generally, the T_g of the laminate is from 130°C to 220°C, and preferably from 140°C to 190°C, and more preferably from 150°C to 190°C.

Laminates prepared using the epoxy resin composition of the invention also tend to exhibit high T_d values, although these can vary significantly depending on
15 the choice of particular starting materials. T_d stands for temperature of thermal degradation measured by thermal gravimetric analysis (TGA). The sample is heated at a rate of 10°C/min, and the weight of the sample is followed. The T_d value is the temperature at which the sample has lost 5 weight percent of its original weight.

In many cases, T_d values of from 300°C to 400°C, preferably from 320°C
20 to 380°C and more preferably 330°C to 370°C, can be obtained.

T_{260} is determined by thermogravimetric analysis (TMA). The sample is heated to 260°C and held at that temperature until such time as a measureable change in sample thickness, as a result of thermal decomposition, is detected. T_{260}
values are preferably at least 15 minutes, more preferably at least 30 minutes and
25 especially 60 minutes or more. T_{288} is measured in the same way, except the sample is heated to 288°C. T_{288} values of 5 minutes or more are preferred.

Solder dip is a rapid test that provides an indication of how an electrical laminate will withstand soldering conditions. The laminate is dipped into molten lead-free solder at 288°C. The sample is held in the solder until delamination is
30 caused by decomposition of the resin. The time at which decomposition begins is the solder dip value. Solder dip values of at least 100 seconds are preferred.

This invention also permits laminates to be formed having very low dielectric properties, as indicated by D_k and D_f . Laminates made in accordance with

the invention often exhibit a D_k of less than 4.3, preferably less than 4.2 and more preferably less than 4.0 at 1 MHz. The D_r of the laminate is often less than 0.020, preferably less than 0.015 and more preferably less than 0.010, at 1 MHz.

5 Laminates made in accordance with the invention also tend to resist delamination.

 The halogenated oligomer of the invention can also be used as a component in an adhesive coating for metallic foils, such as copper foils. In one embodiment, the coating composition includes the halogenated oligomer, at least one epoxy resin and at least one epoxy curing agent. In another embodiment, the coating
10 composition includes an advanced, halogenated epoxy resin as described above, optionally at least one additional epoxy resin, and at least one epoxy curing agent. Methods for applying and curing coatings onto metal foils are described, for example, in U. S. Patent No. 6,432,541.

 The present invention will be described in more detail with reference to
15 the following Examples and Comparative Samples, which are not to be construed as limiting. Unless otherwise indicated, all parts and percentages are by weight.

 Various terms and designations for the materials used in the following Examples are explained as follows:

 D.E.R.® 330 epoxy resin is a diglycidylether of bisphenol A with an
20 epoxy equivalent weight (EEW) of 180, commercially available from The Dow Chemical Company.

 D.E.N.® 438 is a phenol novolac epoxy resin having epoxy equivalent weight of 180, commercially available from The Dow Chemical Company.

 D.E.R.® 560 is a brominated diglycidyl ether of bisphenol A having an
25 epoxy equivalent weight of 452, available from The Dow Chemical Company.

 D.E.R.® 592A80 is a brominated advanced epoxy resin, commercially available from The Dow Chemical Company.

 "TBBA" stands for tetrabromobisphenol-A.

 D.E.R.® 542 is a brominated epoxy resin having an epoxy equivalent
30 weight of 330, commercially available from The Dow Chemical Company.

 SD 500 C is a bisphenol A novolac, sold by Borden Chemical Company.

DOWANOL® PMA is a propylene glycol monomethyl ether acetate, commercially available from The Dow Chemical Company.

DOWANOL® PM is a propylene glycol monomethyl ether, commercially available from The Dow Chemical Company.

5 Various experimental testing and analytical methods used for various measurements in the following Examples are as follows:

DSC stands for differential scanning calorimetry. T_g is the mid point T_g by DSC, measured using a heating rate is 10°C/minute for films and 20°C/minute for laminates.

10 DMTA stands for dynamic mechanical thermal analysis. T_g is measured at a heating rate of 10°C/minute to 280°C with a oscillation rate of 10 Hz.

The stroke cure reactivity of resins is measured by blending the resin solution with a catalyst and a hardener and reacting them on the surface of a 170°C hot plate. Reactivity is reported as the elapsed time required for gelation.

15 Examples 1 and 2 and Comparative Examples A and B

Oligomer Example 1 was prepared by charging 28.8 parts of D.E.R.® 542 epoxy resin, 71.2 parts of TBBA and 42.8 parts of DOWANOL® PMA to a 1 liter glass reactor equipped with a mechanical stirrer, a heating jacket, a nitrogen inlet and a condenser. The reactor contents were heated to 110°C to form a resin solution. 1500
20 ppm of ethyltriphenylphosphonium acetate catalyst, based on the combined weight of the epoxy resin and TBBA, was added to the resin solution. The solution was then heated to 130°C and held at that temperature until the epoxy content was reduced to less than 0.5 percent (approximately 90-120 minutes). Additional DOWANOL® PMA was added to cool the resulting resin solution. The ratio of phenolic groups to residual
25 epoxide groups in Oligomer Example A was approximately 20:1.

Oligomer Example 2 was prepared in the same manner, except for the proportions of starting materials, which were as indicated in Table 1. The ratio of phenolic groups to residual epoxide groups in Oligomer Example A was in excess of 20:1.

30 Comparative Sample A was prepared in by charging 28.8 parts of D.E.R.® 542 epoxy resin and 71.2 parts TBBA to the reactor. The reaction mixture was heated to 150°C and stirred under a nitrogen atmosphere until a transparent liquid formed. 1500 ppm of ethyltriphenylphosphonium acetate catalyst was added, with the

temperature being controlled to below 170°C during the catalyst addition. The mixture was then cooled to 150°C and held at that temperature for one hour. The brominated phenolic oligomer was then cooled and flaked as a solid.

Comparative Sample B was prepared in the same manner as

- 5 Comparative Sample A, except for the proportions of starting materials, which were as indicated in Table 1.

The phenolic equivalent weight, melt viscosity at 150°C, T_g (by DSC), solubility in the DOWANOL® PMA solvent, molecular weights and product distribution were determined for each of Examples 1 and 2 and Comparative Samples

10 A and B. Results were as indicated in Table 1.

Table 1

Components	Example 1	Comparative Sample A*	Example 2	Comparative Example B*
D.E.R. 542, pbw ¹	28.8	28.8	37.75	37.75
TBBA, pbw ¹	71.2	71.2	62.25	62.25
DOWANOL PMA, pbw ¹	42.8	0	70	0
Phenolic E.W.	542	563	874	873
T _g , °C	62 ⁴	80	88 ⁴	99
Solubility ²	Soluble	Partially soluble	Soluble	Partially soluble
M _n	811	822	1194	1185
M _w	1501	1735	2542	2797
M _z	2571	3254	4428	5097
Polydispersity	1.85	2.11	2.13	2.36
Free TBBA, wt-percent	35	36	18	20
2:1 Adduct ³ , wt-percent	33	26	25	22
2:2 Adduct ³ , wt-percent	20	19	23	20
4:3 Adduct ³ wt-percent	8	10	15	15
Highers	4	9	19	23
Melt Viscosity @ 150°C, Pa	3.8 ⁴	10.4	65 ⁴	>100 ⁵

*Not an example of the invention. ¹Parts by weight of respective starting materials. ²Solubility in ethylene glycol monomethyl ether acetate. "Soluble" means a clear solution was obtained at room temperature. "Partially soluble" indicates that a turbid solution that partially phase separates over time was obtained at room temperature. ³A 2:1 adduct was the reaction product of 1 mole of epoxy resin and 2 moles of TBBA. A 3:2 adduct was the reaction product of 2 moles of epoxy resin and 3 moles of TBBA. A 4:3 adduct was the reaction product of 3 moles of epoxy resin with 4 moles of TBBA. Highers were 5:4 and higher adducts. ⁴Evaluated after drying the oligomer composition for 2 hours at 150°C followed by drying for 1 hour under vacuum. ⁵Sample was too viscous to measure accurately at this temperature.

The results summarized in Table 1 show how the method of oligomer preparation affects the composition and properties of the oligomer. M_n and phenolic equivalent weight remain essentially unchanged, whereas M_w, M_z and polydispersity are all reduced. Viscosity is also reduced significantly. The solvent preparation process used to produce Examples 1 and 2 produces lower amounts of higher molecular weight (4:3) adducts that are formed. The T_g of the oligomer is also lower when it is produced in the solvent preparation process.

Examples 3-10

Oligomer Example 3 was prepared in the same general manner described with respect to the preparation of halogenated oligomer Examples 1 and 2, using proportions of starting materials as indicated in Table 2.

5 Oligomer Example 4 was prepared in the same manner as Oligomer Examples 1 and 2, except that after the TBBA/D.E.R.542 mixture had reacted, a small quantity of a non-halogenated epoxy resin, D.E.R.® 330, was added and allowed to react to increase the molecular weight of the oligomer. Proportions of starting materials were as indicated in Table 2.

10 Oligomer Example 5 was prepared in the same manner as Oligomer Example 4, using proportions of starting materials as indicated in Table 2.

Oligomer Example 6 was prepared in the same general manner described with respect to Examples 1 and 2, using proportions of starting materials as indicated in Table 2.

15 Oligomer Examples 7 and 8 were prepared in the same general manner described with respect to Examples 1 and 2, except that a mixture of D.E.R.® 542 and a non-halogenated epoxy resin (D.E.R.® 330) was used to make the oligomer. Proportions of starting materials were as indicated in Table 2.

Oligomer Example 9 was prepared by charging D.E.R.® 560
20 halogenated epoxy resin, TBBA and propylene glycol monomethyl ether (DOWANOL® PM from The Dow Chemical Company) to a 1 liter glass reactor equipped with a mechanical stirrer, a heating jacket, a nitrogen inlet and a condenser. The reactor contents were heated to 90°C to form a resin solution. 1500 ppm of
25 ethyltriphenylphosphonium acetate catalyst, based on the combined weight of the epoxy resin and TBBA, was added to the resin solution. The solution was then heated to 110°C and held at that temperature until the epoxy content was reduced to less than 0.5 percent (approximately 240-300 minutes). Proportions of starting materials were as indicated in Table 2.

Oligomer Example 10 was made in the same manner as Oligomer
30 Example 9, except that a small amount of a nonhalogenated resin (D.E.R.® 330) was added with the other reactants. Proportions of starting materials were as indicated in Table 2.

After the oligomer composition was formed in each case, D.E.N 438 epoxy novalac resin was added in the amount indicated in Table 2, and the mixture

was heated to 110°C. Ethyltriphenylphosphonium acetate catalyst was added in the amounts indicated in Table 2, and the mixture was heated to 140°C (110°C for Examples 9 and 10) and held at that temperature until the indicated epoxy equivalent weight was obtained. Additional solvent was then added as indicated in Table 2.

- 5 The equivalent weight, bromine content and percent solids of the resulting advanced resins were as indicated in Table 2.

Table 2

Ex. No.	3	4	5	6	7	8	9	10
<u>Oligomer Preparation</u>								
D.E.R. 542, pbw	10.07	6.32	7.9	5.87	7.039	10.06	0	0
D.E.R. 330, pbw	0	5.19	2.2	0	2.10	3.14	0	0.587
D.E. R. 560, pbw	0	0	0	0	0	0	7.04	7.42
TBBA, pbw	12.44	15.62	13.0	14.51	13.57	19.48	12.63	13.3
DOWANOL PMA, pbw	5.63	7.37	7.0	6.8	13.34	19.5	0	0
DOWANOL PM, pbw	0	0	0	0	0	0	4.94	5.32
Catalyst	0.045	0.045	0.045	0.03	0.03	0.045	0.03	0.03
<u>Advancement Reaction</u>								
D.E.N. 438	52.43	53.6	57.7	53.8	53.90	37.32	62.3	60.65
Catalyst	0.04	0.04	0.04	0.0375	0.04	0.04	0.04	0.04
DOWANOL PMA	19.35	6.9	0	4.95	0	0	0	0
Acetone	0	5	12.2	14	10.16	10	0	0
DOWANOL PM	0	0	0	0	0	0	13.1	12.7
<u>Advanced Resin properties</u>								
EEW	272	282	280	286	276	381	260	266
Bromine content, wt percent based on solids	16	15	14	15	15.1	23	13.3	14.0
Solid content, percent	75	80	80	75	75	70	80	80

- Varnishes were prepared by separately blending advanced epoxy resin
- 10 Examples 3-10 with a hardener solution, boric acid solution and catalyst solution for 60 minutes at room temperature. The hardener solution was prepared by blending dicyandiamide (10 weight percent) at room temperature with DOWANOL™ PM (45 weight percent) and dimethylformamide (45 weight percent). The boric acid solution
- 15 was prepared by blending boric acid (20 weight percent) at room temperature with methanol (80 weight percent). The catalyst solution was prepared by blending 2-ethyl, 4-methyl imidazole (20 weight percent) or 2-phenylimidazole (20 weight percent) at room temperature with methanol (80 weight percent). The bisphenol A novolac solution was prepared by blending (43 percent) of the bisphenol A novolac resin with

DOWANOL® PMA (28.5 weight percent) and methyl ethyl ketone (28.5 weight percent) at room temperature. The varnishes prepared using advanced epoxy resins 6, 9 and 10 further include tetraphenolethane (1,1,2,2-tetra-(4-hydroxyphenyl)-ethane). Varnish Examples 3-2, 7 and 8 were cured using a bisphenol A novolac (SD-500 C from Borden Chemical) resin solution instead of the dicyandiamide hardener solution. Proportions of the various ingredients used to make the varnishes were as indicated in Table 3.

The reactivity of the varnish was evaluated by heating the varnish on the surface of a 171°C hot plate, and measuring the time required for the varnish to gel. Results were as indicated in Table 3.

For comparison, a varnish (Comparative Sample C-1) was prepared using 100 parts by weight of a commercial brominated, advanced epoxy resin. The varnish also contained 3.2 parts of dicyandiamide and 0.1 parts of 2-ethyl-4-methyl imidazole. The reactivity of this varnish was as indicated in Table 3.

Table 3

Varnish Sample No.	3-1	3-2	4-1	5-1	6-1	7-1	8-1	9-1	10-1	Comp. Sample C-1*
<u>Components (pbw, solids basis)</u>										
Advanced Resin Example 3	100	100	0	0	0	0	0	0	0	0
Advanced Resin Example 4	0	0	100	0	0	0	0	0	0	0
Advanced Resin Example 5	0	0	0	100	0	0	0	0	0	0
Advanced Resin Example 6	0	0	0	0	100	0	0	0	0	0
Advanced Resin Example 7	0	0	0	0	0	100	0	0	0	0
Advanced Resin Example 8	0	0	0	0	0	0	100	0	0	0
Advanced Resin Example 9	0	0	0	0	0	0	0	71.43	0	0
Advanced Resin Example 10	0	0	0	0	0	0	0	0	71.92	0
D.E.R. 592 A 80	0	0	0	0	0	0	0	0	0	100
Boric acid	0.5	0	0.25	0.25	0.3	1.76	0.39	0.571	0.575	0
Bis A Novolac	0	0	0	0	0	100	43	0	0	0
Dicyandiamide	4	0	4	4	4	0	0	0	0	3.2
Bisphenol A novolac	0	45.1	0	0	0	74.87	54.85	0	0	0
Phenol novolac resin	0	0	0	0	0	0	0	24.75	25.2	0
Tetraphenol ethane	0	0	0	0	1.1	0	0	2.75	2.8	0
TBBA	0	0	0	0	0	45.23	0	0	0	0
2ethyl-4-methyl imidazole	0.15	0.05	0.13	0.16	0.12	0	0	0	0	0.1
2-methyl imidazole	0	0	0	0	0	0	0	0.08	0.08	0
2-Phenylimidazole	0	0	0	0	0	0.48	0.29	0	0	0
Gel time at 170°C, s	211	212	245	250	217	276	235	233	211	265

*Not an example of the invention.

5

Prepregs were prepared from the above varnish formulations by a dipping method, using a substrate of glass cloth (Type 7628 from Porcher Textile, Badinieres, Fr-38300 Bourgoin-Jallieu France or Interglas Textil GmbH, Ulm/Donau, Germany). The impregnated substrates were passed through a CARATSCH™ pilot treater (built by Caratsch AG, Bremgarten, Switzerland) having a 3 meter horizontal

oven, at an air temperature of from 170 to 175°C and a winding speed of from 1 to 1.6 meters per minute.

The resin content of each prepreg was measured by weighing 10 cm x 10 cm square sheets of glass cloth before and after prepreg production, according to
5 Method IPC-L-109B, IPC-TM-650:2.3.16 (available from the Institute for Interconnecting and Packaging Electronic Circuits, Lincolnwood, Illinois, USA.). The results were as shown in Table 4 below.

Eight sheets of each prepreg were laid-up in alternating layers with sheets of copper foil on outer layers, and then heated under pressure to form an
10 electrical laminate. The properties of the laminates were as indicated in Table 4 below.

Table 4

Ex. No.	3-3	3-4	4-2	5-2	6-2	7-2	8-2	9-2	10-2	C-2*
Prepreg properties										
Residual gel time, s	46	57	62	30	89	33	64	79	67	113
Resin content, percent	50	47	45	43	40.8	70	95	46	44	46
Laminate properties										
Laminating conditions, °C/min	190/90	190/90	185/60	190/60	185/60	206/90	220/90	200/90	200/90	190/60
Thickness, (mm)	1.67	1.61	1.69	1.63	1.75	1.68	1.72	1.64	1.62	1.65
T _g by DSC, °C	185/180	152/157	167/169	174/178	172/177	196/198	172/173	176/174	173/173	166/164
T _g by DMTA, °C	218	180	201	214	203	ND	213	ND	ND	190
T ₂₆₀ , min.	19	>70	27	30	18	>60	>60			8
T ₂₈₈ , min	ND	ND	ND	ND	ND	ND	ND	41	41	ND
T ₃₀₀ , min.	ND	ND	ND	ND	ND	22.6	17	ND	ND	ND
Solder dip at 288°C, s	106	310	109	102	ND	ND	>300	ND	ND	50
T _d by TGA, °C	317	369	325	321	317	362	361	362	361	285
Copper peel strength, (N/cm)	16	14	15	15	18	14	12.3	13.9	14.9	15
Pressure cooker test, 180 minutes, pass rate (water absorption)	100 percent	100 percent	ND	ND	ND	100 percent pass (0.34)	100 percent (0.3)	100 percent passed 120 min. (0.36)	100 percent passed 120 min. (0.36)	100 percent passed 120 min. (0.36)
UL 94 rating	V-0	V-0	V-0	V-0	V-0	V-0 (14 s)	V-0 (23 s)	ND	V-0	V-0
D _k (1 MHz)	ND	ND	ND	ND	ND	ND	4.2	ND	ND	4.6
D _k (1 GHz)	ND	ND	ND	ND	ND	ND	3.9	ND	ND	4.3
D _r (1 MHz)	ND	ND	ND	ND	ND	ND	0.0129	ND	ND	0.0146
D _r (1 GHz)	ND	ND	ND	ND	ND	ND	0.0164	ND	ND	0.0120

*Not an example of the invention. ND = not determined.

The data in Table 4 shows that the preregs and laminates made from the compositions of the present invention exhibited much better thermal stability (T₂₆₀, solder dip, T_d) than those made from the Comparative Example. Cured laminate T_g was higher for Examples 3-3 and 4-2 through 10-2 than for the Comparative Sample. That of Sample 3-2 is somewhat lower than the T_g of the Comparative Sample, due to the use of a different hardener. Note that the T_g of Examples 7-2 and 8-2 exceeded that of the Comparative Sample despite the use of the different hardener.

Example 11

Oligomer Example 11 was prepared by charging 752.8 parts of D.E.R.® 560 epoxy resin, 1350.2 parts of TBBA and 1402 parts of DOWANOL® PM to a 10 liter steel reactor equipped with a mechanical stirrer, a heating jacket, a nitrogen inlet and a condenser. The reactor contents were heated to 100°C to form a resin solution. 3.1 parts of ethyltriphenylphosphonium acetate catalyst, based on the combined weight of the epoxy resin and TBBA, was added to the resin solution. The solution is then heated to 110°C and held at that temperature for 50 minutes until the epoxy content was reduced to 2.5 percent based on the weight of the reactive starting materials. The solution was then cooled to 60°C to produce a solution Oligomer Example 11. The ratio of phenolic groups to residual epoxide groups in Oligomer Example 11 was approximately 3.75:1.

7554.8 parts of an 85 percent by weight solution of D.E.N.® 438 epoxy novalac in DOWANOL® PM was added to the solution of Oligomer Example 11. The resulting mixture was heated to 110°C and held at that temperature for 2.5 hours until the epoxy content was reduced to 15.8 percent, based on reactive starting materials. Another 56.2 parts of DOWANOL® PM solvent was then added, and the resulting solution of advanced epoxy resin was cooled to 35-40°C.

A varnish was prepared by blending advanced epoxy resin Example 11 with a hardener solution, boric acid solution and catalyst solution for 60 minutes at room temperature. The hardener solution was prepared by blending a phenol novolac resin, tetraphenolethane, methyl ethyl ketone and DOWANOL® PM at a 54:6:20:20 weight ratio. The boric acid solution was prepared by blending boric acid (20 weight percent) at room temperature with methanol (80 weight percent). The catalyst solution was prepared by blending 2-ethyl imidazole (20 weight percent) with methanol (80 weight percent). The advanced epoxy resin solution, hardener solution,

boric acid solution and catalyst solution were mixed at a 71.92:27.5:0.58:0.105 weight ratio.

The reactivity of the varnish was evaluated by heating a sample of the varnish on the surface of a 170°C hot plate, and measuring the time required for the varnish to gel. Under these conditions, the varnish gelled in 194 seconds.

Prepregs and laminates were prepared using the varnish, in the manner described with respect to Examples 3-10. The prepreg gel time was 56 seconds. The T_g of the laminate was 175-178°C. The T_d at 5 percent weight loss temperature was 358°C and the T_{288} time was 28 minutes.

10 Example 12

Oligomer Example 11 was prepared by charging 896.5 parts of D.E.R.® 560 epoxy resin, 1071.8 parts of TBBA and 1312.2 parts of DOWANOL® PM to a 10 liter steel reactor equipped with a mechanical stirrer, a heating jacket, a nitrogen inlet and a condenser. The reactor contents were heated to 100°C to form a resin solution. 2.95 parts of ethyltriphenylphosphonium acetate catalyst, based on the combined weight of the epoxy resin and TBBA, was added to the resin solution. The solution was then heated to 110°C and held at that temperature for 65 minutes until the epoxy content is reduced to 3 percent based on the weight of the reactive starting materials. The solution is then cooled to 60°C to produce a solution Oligomer Example 12. The ratio of phenolic groups to residual epoxide groups in Oligomer Example 12 was approximately 2.5:1.

6422.5 parts of an 85 percent by weight solution of D.E.N.® 438 epoxy novalac in DOWANOL® PM was added to the solution of Oligomer Example 11. The resulting mixture was heated to 110°C and held at that temperature for 2.5 hours until the epoxy content was reduced to 15.8 percent, based on reactive starting materials. The resulting solution of advanced epoxy resin was cooled to 35-40°C.

A varnish was prepared by blending advanced epoxy resin Example 12 with a hardener solution, boric acid solution and catalyst solution for 60 minutes at room temperature. The hardener solution was prepared by blending a bisphenol A novalac resin, tetraphenolethane, methyl ethyl ketone and DOWANOL® PM at a 54:6:20:20 weight ratio. The boric acid solution and catalyst solutions were prepared as described in Example 11. The advanced epoxy resin solution, hardener solution, boric acid solution and catalyst solution were mixed at a 69:31:0.548:0.15 weight ratio.

The reactivity of the varnish was evaluated by heating a sample of the varnish on the surface of a 170°C hot plate, and measuring the time required for the varnish to gel. Under these conditions, the varnish gelled in 217 seconds.

- 5 Prepregs and laminates were prepared using the varnish, in the manner described with respect to Examples 3-10. The prepreg gel time was 77 seconds. The T_g of the laminate was 181-183°C. The T_d at 5 percent weight loss temperature was 352°C and the T_{288} time was 24 minutes.

CLAIMS

1. A process comprising forming a reaction mixture containing a stoichiometric excess of at least one halogenated epoxide-reactive compound and at least one halogenated epoxy resin in the presence of a solvent, and subjecting the reaction mixture to conditions sufficient to consume the epoxy groups of the halogenated epoxy resin to form a solution of an oligomer composition in the solvent, wherein the oligomer composition has a number average molecular weight of from 700 to 3200 and a weight average molecular weight of from 1500 to 7000 and contains at least 2.0 terminal epoxide-reactive groups per molecule.
2. The process of claim 1 wherein the halogenated epoxide-reactive compound contains at least one bromine atom.
3. The process of claim 2 wherein the halogenated epoxy resin contains at least one bromine atom.
4. The process of claim 3 wherein the halogenated epoxide-reactive compound is a phenolic compound having at least 2 epoxide-reactive groups and at least one bromine atom bonded to a carbon atom on an aromatic ring.
5. The process of claim 4 wherein the halogenated epoxy resin contains at least one bromine atom bonded to a carbon atom of an aromatic ring.
6. The process of claim 1 wherein the reaction mixture further contains at least one non-halogenated epoxy resin.
7. The process of claim 6 wherein at least 95% by weight of the epoxy resins in the reaction mixture contain 2 epoxy groups/molecule.
8. The process of claim 7 wherein at least 95% by weight of the epoxide-reactive compounds in the reaction mixture contain 2 phenol groups/molecule.
9. The process of claim 1 wherein the reaction mixture further contains at least one non-halogenated epoxy-reactive compound.
10. The process of claim 1 wherein the oligomeric composition contains from 10 to 60% by weight halogen atoms.
11. The process of claim 10 wherein the halogenated epoxide-reactive compound is a brominated bisphenol, and the halogenated epoxy resin is a diglycidyl ether of a halogenated bisphenol.

12. The process of claim 1 wherein the solvent constitutes from 10 to 75% of the combined weight of the solvent, epoxide-reactive compound(s) and epoxy resin(s).
13. The process of claim 1, further comprising mixing the oligomer solution with at least one additional epoxy resin and subjecting the mixture to conditions sufficient to form an advanced, halogenated epoxy resin.
14. The process of claim 13, wherein the additional epoxy resin is not halogenated.
15. The process of claim 14, wherein the additional epoxy resin has an average functionality of at least 2.0 epoxide groups per molecule.
16. The process of claim 15, wherein the additional epoxy resin is a glycidyl ether of a polyhydric phenol compound, a diglycidyl ether of an aliphatic glycol, a diglycidyl ether of a polyether glycol, a cresol-formaldehyde novolac epoxy resin, a phenol-formaldehyde novolac epoxy resin, a bisphenol A novolac epoxy resin, tris(glycidyloxyphenyl)methane, tetrakis(glycidyloxyphenyl)ethane, or a mixture of any two or more thereof.
17. The process of claim 16, wherein the additional epoxy resin is a glycidyl ether of resorcinol, catechol, hydroquinone, bisphenol, bisphenol A, bisphenol AP, bisphenol F or bisphenol K.
18. The process of claim 16 further comprising curing the advanced, halogenated epoxy resin by reacting it with at least one epoxy curing agent.
19. The process of claim 13 further comprising curing the advanced, halogenated epoxy resin by reacting it with at least one epoxy curing agent.
20. A varnish comprising a solution of an advanced, halogenated epoxy resin produced in accordance with claim 13, and at least one epoxy curing agent.
21. The varnish of claim 20, further comprising at least one other epoxy resin.
22. The varnish of claim 21, further comprising boric acid or a boron ester.
23. A prepreg comprising a substrate material impregnated with the varnish of claim 22.
24. A prepreg comprising a substrate material impregnated with the varnish of claim 20.
25. The varnish of claim 21, wherein the additional epoxy resin used to make the halogenated, advanced epoxy resin is a glycidyl ether of a polyhydric phenol compound, a diglycidyl ether of an aliphatic glycol, a diglycidyl ether of a polyether glycol, a cresol-formaldehyde novolac

epoxy resin, a phenol-formaldehyde novolac epoxy resin, a bisphenol A novolac epoxy resin, tris(glycidyloxyphenyl)methane, tetrakis(glycidyloxyphenyl)ethane, or a mixture of any two or more thereof.

26. A varnish comprising a solution of an oligomer composition produced in accordance with claim 1, an epoxy resin, and at least one epoxy curing agent.

27. A prepreg comprising a substrate material impregnated with the varnish of claim 26.