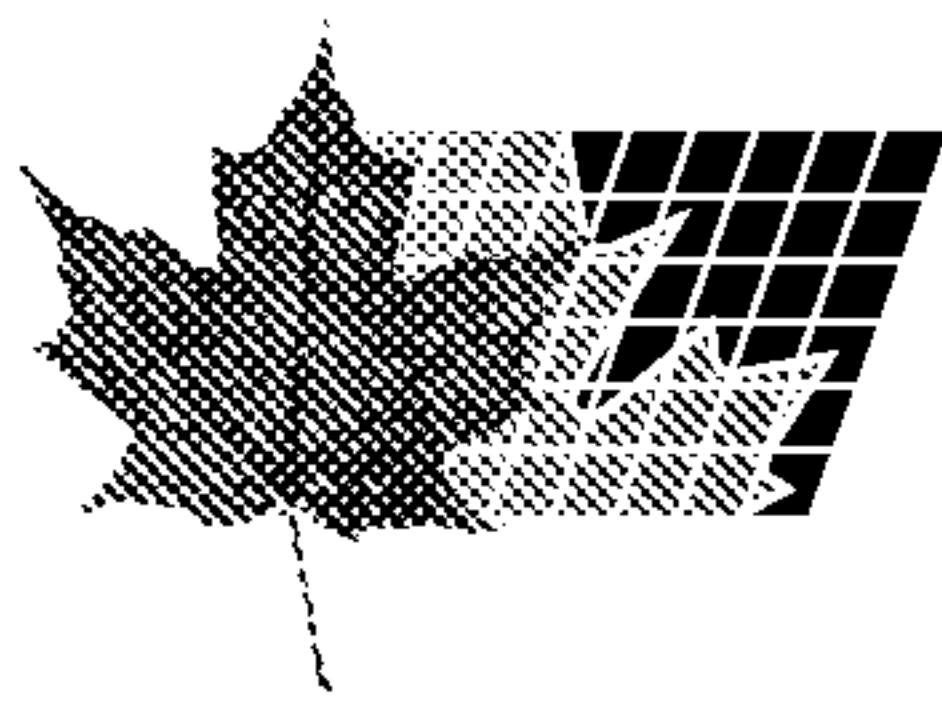




(72) GERBER, ARTHUR H., US

(71) BORDEN CHEMICAL, INC., US

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(54) **NOVOLAQUES A BASE DE PHENOL, A PROPRIETES
OPTIQUES AMELIOREES**

(54) **PHENOL-NOVOLACS WITH IMPROVED OPTICAL
PROPERTIES**

(57) Procédé de préparation d'un produit polyphénolique fluorescent à haute absorbance des UV, son époxydation ultérieure, ainsi que produits polyphénoliques et dérivés époxydés et compositions contenant lesdits produits et dérivés. Lesdits produits polyphénoliques sont préparés par chauffe de glyoxal à une température d'environ 80 °C à environ 100 °C avec un excédent molaire de phénol en présence d'un catalyseur acide qui est éliminé du mélange de réaction à une température d'environ 170 °C. Le rapport molaire total du glyoxal au phénol introduit dans le mélange de réaction est d'environ 0,15 à 0,22 mole de glyoxal pour chaque mole de phénol. Le glyoxal est ajouté au phénol en continu ou par étapes de manière que les unités aldéhyde dans le mélange de réaction soient maintenues à moins d'environ 70 % des unités aldéhyde présentes dans la quantité totale de glyoxal à introduire pour préparer le polyphénol. De l'eau est distillée par étape ou en continu du mélange de réaction. Le catalyseur est éliminé du mélange de réaction par une nouvelle distillation du mélange de réaction, en général à des températures plus élevées.

(57) The specification discloses a method for the manufacture of a fluorescent polyphenolic product with high UV absorbance, its subsequent epoxidation as well as polyphenolic products and epoxidized derivatives and compositions thereof. The polyphenolic products are prepared by heating glyoxal at a temperature of about 80 °C to about 100 °C with a molar excess of a phenol in the presence of an acidic catalyst which is eliminated from the reaction mixture at a temperature about 170 °C. The total mole ratio of glyoxal to phenol charged to the reaction mixture is about 0.15 to 0.22 moles of glyoxal for each mole of phenol. The glyoxal is added continuously or by stepwise additions to the phenol so as to keep the aldehyde units in the reaction mixture to less than about 70% of the aldehyde units in the total quantity of glyoxal to be charged for making the polyphenol. Water is distilled stepwise or continuously from the reaction mixture. The catalyst is removed from the reaction mixture by further distilling the reaction mixture, generally at higher temperatures.

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(21) International Application Number: PCT/US99/04799 (22) International Filing Date: 5 March 1999 (05.03.99) (30) Priority Data: 09/158,584 22 September 1998 (22.09.98) US (71) Applicant: BORDEN CHEMICAL, INC. [US/US]; Kenneth P. Van Wyck, 180 East Broad Street, Columbus, OH 43215 (US). (72) Inventor: GERBER, Arthur, H.; 260 Wakefield Trace, Louisville, KY 40245 (US). (74) Agent: MASKAS, George, P.; 3361 Stonehenge Court, Columbus, OH 43221 (US).		(81) Designated States: AU, BR, CA, CN, IN, JP, KR, MX, NO, RU, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>With amended claims and statement.</i>
(54) Title: PHENOL-NOVOLACS WITH IMPROVED OPTICAL PROPERTIES (57) Abstract The specification discloses a method for the manufacture of a fluorescent polyphenolic product with high UV absorbance, its subsequent epoxidation as well as polyphenolic products and epoxidized derivatives and compositions thereof. The polyphenolic products are prepared by heating glyoxal at a temperature of about 80 °C to about 100 °C with a molar excess of a phenol in the presence of an acidic catalyst which is eliminated from the reaction mixture at a temperature about 170 °C. The total mole ratio of glyoxal to phenol charged to the reaction mixture is about 0.15 to 0.22 moles of glyoxal for each mole of phenol. The glyoxal is added continuously or by stepwise additions to the phenol so as to keep the aldehyde units in the reaction mixture to less than about 70% of the aldehyde units in the total quantity of glyoxal to be charged for making the polyphenol. Water is distilled stepwise or continuously from the reaction mixture. The catalyst is removed from the reaction mixture by further distilling the reaction mixture, generally at higher temperatures.		

PHENOL-NOVOLACS WITH IMPROVED OPTICAL PROPERTIES

This invention relates to phenolic-glyoxal
5 condensates, glycidylated derivatives thereof, compositions
containing the condensates and their glycidylated
derivatives, as well as methods for manufacture of the
foregoing.

10 In the methods for making the condensates of this
invention, a molar excess of phenol is reacted with glyoxal
at a temperature of about 80° C to 100° C using an acid
catalyst which can be removed from the reaction mixture by
distillation at a temperature below that of about 170° C.

15

The reaction is conducted by making continuous or at
least two additions of glyoxal to a phenol wherein the
total molar ratio for all additions of glyoxal to phenol is
about 0.15 to 0.22. Water in the reaction mixture is
20 removed incrementally by distillation during the reaction.

Less than about 70% of the total glyoxal to be reacted
with the phenol is added to the reaction mixture at any one
time. Also, less than about 70% of the total aldehyde units
25 to be supplied to the reaction mixture together with any
ketone units formed in the reaction are present in the
reaction mixture at any one time. Each glyoxal molecule
contains two aldehyde units. A way for measuring the
aldehyde units together with any ketone units formed is by
30 determining aldehyde equivalents, as later defined. The
aldehyde equivalents in the reaction mixture are maintained
at less than about 70% of the aldehyde equivalents in the
total quantity of glyoxal to be charged to the reaction
mixture for making the condensation product. The catalyst
35 is removed from the reaction mixture when at least about
85% of the aldehyde equivalents or aldehyde units in the
total quantity of glyoxal to be charged to the reaction

mixture for making the condensation product have reacted. Removal of the catalyst also eliminates all or a portion of the water in the reaction mixture. After about 85% of the said aldehyde equivalents have reacted and prior to removal
5 of the catalyst, in those cases where trichloroacetic acid is the catalyst, a sufficient quantity of a basic material is added to the reaction mixture to neutralize HCl to be liberated by the trichloroacetic acid. After removal of the catalyst, the reaction mixture is heated at a temperature
10 of from about 175° C to 200° C for about 0.25 hours to 3 hours. Also, after removal of the catalyst, any remaining unreacted phenol as well as water is removed at temperatures above that used for removal of the catalyst.

15 BACKGROUND AND PRIOR ART

Polyphenols, such as polyphenols prepared from the condensation of glyoxal and a molar excess of phenol in the presence of an acid catalyst, find utility in the same
20 manner as other polyphenols and particularly for preparing epoxidized polyphenols which can be used for coatings and electronic applications as well as adhesives and laminates in the production of printed circuit boards.

25 The polyphenols of this invention will typically contain from about 1% to about 6% of the tetraphenols of ethane. When the phenol is phenol itself, the tetraphenol is tetrakis(p-hydroxyphenyl) ethane which is also referred to as TPE. Although the reaction products of the phenol-
30 glyoxal reaction are mixtures, individual polyphenols such as TPE as well as other components thereof can be crystallized out of solution by conventional techniques. Thus, the level of tetraphenol ethanes, such as TPE in the phenol-glyoxal condensation products, can be greatly
35 reduced to essentially zero by methods well known in the art without sacrifice of desirable optical properties provided by this invention. Illustratively, use of

solvents such as alcohol-aromatic hydrocarbon mixtures and water miscible ketone-water mixtures are effective in this regard.

5 The compositions of this invention are particularly useful when automatic optical inspection (AOI) is used for quality control of laminates. The polyphenols of this invention alone, or in blends with phenolic novolacs, or after epoxidation of the polyphenols, are useful for AOI
10 as are adducts with epoxy resins and adducts of epoxidized phenolic-glyoxal condensates with phenolic novolacs. The AOI is typically performed by measuring: fluorescence at wavelengths in the range of about 450 nm (nanometers) to about 650 nm, particularly at an excitation wavelength of
15 about 442 nm; and/or ultraviolet (UV) light absorbance in the wavelengths of from about 350 to 365 nm.

Applicant has found a set of process conditions together with monomers and certain catalysts for obtaining
20 polyphenols and epoxidized derivatives thereof having UV absorbance and/or fluorescence which is substantially higher than phenol-glyoxal condensates prepared by other methods within the wavelengths generally used for AOI quality control. Photoimageable materials are used in
25 conjunction with these condensates. High UV absorbance is desirable for the manufacture of laminates used in electronic applications such as high density multilayer printed circuit boards.

Advantages of this invention include: (a) preparation
30 of an essentially metal ion-free polyphenol without recourse to catalyst filtration or neutralization and water washing steps wherein recovery of phenol is simplified and the reactor yield is increased in those cases where the catalyst is not neutralized with a metal ion; (b)
35 preparation of polyphenols as well as the epoxidized derivatives thereof which exhibit improved optical properties, e.g., high fluorescence and/or UV absorbance in

the wavelengths used for AOI; and (c) preparation of polyphenols with increased solubility in organic solvents.

The prior art discloses many methods for making polyphenols and epoxidized derivatives thereof. But the prior art does not use the combination of monomers, reaction conditions, or catalyst which applicant uses for obtaining the desirable properties of the products of this invention. Also, the prior art does not disclose phenol-glyoxal condensates having the desirable optical properties of this invention.

As used herein, the following terms have the following meanings:

(a) "phenol-glyoxal condensation product" shall refer to the phenol-glyoxal reaction product produced by the method of this invention wherein such condensate contains less than 5% of unreacted phenol, preferably less than 3% of unreacted phenol and particularly less than 1.5% of unreacted phenol.

(b) "aldehyde equivalents" is a method for measuring aldehyde units and shall refer to aldehyde and any ketone units which may be formed in the reaction mixture or in the glyoxal charged or to be charged when measured by the below described method. Such measurements are generally reported in percent of aldehyde equivalents reacted in comparison with the aldehyde equivalents charged or to be charged to the reaction mixture. Thus, if measurements of aldehyde equivalents in a mixture of the glyoxal and phenol charged show X aldehyde equivalents and measurements after reaction in the reaction mixture later show aldehyde equivalents of $1/2$ of X, then the aldehyde equivalents in the reaction mixture are 50% of that charged. During the reaction, some ketone groups may also be formed which are included in measuring of the aldehyde equivalents and are considered as part of the aldehyde equivalents herein.

The method for determining aldehyde equivalents is by taking 1.0 gram of reaction mixture and diluting it with 50 ml of methanol. The pH is then adjusted to 3.5 with dilute sodium hydroxide. There is then added, to the pH adjusted sample, 25 ml of 10% hydroxylamine hydrochloride with stirring. The sample is stirred for 10 minutes and then the sample is back titrated with 0.25 Normal (N) sodium hydroxide to pH of 3.5. The number of milliliters (mls) (the titre) of the sodium hydroxide solution used to back titrate the sample to a pH of 3.5 is used to calculate the aldehyde equivalents. The mls of sodium hydroxide solution in the titre is adjusted by correcting by titration with sodium hydroxide for the methanol and hydroxylamine hydrochloride reagents used in the test and this is referred to as the mls blank.

The aldehyde equivalents for the sample are then determined by the following formula: (2.9 times 0.25 N times (mls sodium hydroxide titre minus the mls of the sodium hydroxide in titrating the blank)). The value obtained by this formula is then compared to the aldehyde equivalents obtained by the above method and formula based on one gram of an unheated, catalyst free mixture of phenol and glyoxal in the weight ratio of glyoxal to phenol used until that time or the time in question in order to determine the percent aldehyde equivalents reacted.

Unless otherwise indicated, the fluorescence measurements herein are as the maximum counts per second for a 0.05% solution of the material in question dissolved in tetrahydrofuran (THF) at an excitation wave length of 442 nm for an acquisition time of one second with a CM 1000 instrument when measured within the range of about 450 to 650 nm. CM 1000 refers to Cure Monitor 1000 which is an instrument made by Spectra Group Ltd., Inc. of Maumee, Ohio. Acquisition time is the exposure time at the designated wavelength. A count is a basic unit used by a

large number of light measuring devices for data output and refers to a process of digitization of accumulated signal. In the case of a CCD detector that is used by Spectra Group Limited, Inc. of Maumee, Ohio and which was used for the data set forth herein, light produces an electrical charge on the detector that is subsequently read out by a digitizer. The digitizer is set to record one count for approximately every 10 units of charge (electrons) it reads.

10

The fluorescence measurements are on a comparative basis among the various materials such as in each of the tables set forth herein and not as absolute numbers. Thus, the fluorescence values of polyphenols within any one of the tables set forth later herein are relative to other polyphenols within the same table, but comparisons cannot be made with the same or other polyphenols in other tables.

20

The UV absorbance values are obtained from samples prepared by dissolving the material in question in THF (tetrahydrofuran) at a concentration of 10 mg (milligrams) per 100 ml (milliliters) and the absorbance measurement made at 350 nm or 365 nm.

25

SUMMARY OF THE INVENTION

In one aspect, this invention is directed to a method for preparing a polyphenolic product by incrementally contacting and reacting glyoxal with a molar excess of phenol in the presence of an acidic catalyst which can be removed from the reaction mixture by distillation at temperatures below about 170° C. A reaction temperature of about 80° C to about 100° C is used for the reaction. Water is removed incrementally from the reaction mixture by distillation while the aldehyde equivalents in the reaction mixture are maintained at less than about 70

percent based on the aldehyde equivalents in the total amount of aldehyde to be charged to the reaction mixture in making the polyphenol. The mole ratio of glyoxal charged to the reaction mixture is from about 0.15 to about 0.22
5 moles of glyoxal for each mole of phenol. The reaction is terminated by distillation to remove the catalyst when at least about 85% of the aldehyde equivalents in the total quantity of glyoxal to be charged for making the condensation product have reacted. When trichloroacetic
10 acid is the catalyst, a basic material is added to the reaction mixture prior to removal of the catalyst to neutralize any hydrochloric acid which may be released during removal of catalyst. Removal of the catalyst also removes some or all of the water in the reaction mixture.
15 After elimination of the catalyst: (a) free or unreacted phenol is distilled out of the reaction mixture so that the product is free of catalyst and contains less than about 5% of phenol; and (b) the reaction mixture is heated at a temperature of from about above 175° C to about 200° C for
20 0.25 to 3 hours.

In another aspect, this invention is directed to a method of preparing a polyphenolic product which comprises: charging and reacting phenol, and about 0.06 to 0.11 moles of a 40% solution of glyoxal in water in the presence of
25 about 2 to 5% of oxalic acid, the moles of glyoxal based on the moles of phenol charged; distilling the reaction mixture a first time to remove about 8% to 12% of distillate after about 1 to 5 hours of reaction time; charging another 0.06 to 0.11 moles of glyoxal based on
30 phenol charged so that the total quantity of glyoxal charged is from about 0.15 to 0.22 moles for each mole of phenol; continuing the reaction for about another 1 to 5 hours from the time the first distillation was commenced, and distilling the reaction mixture a second time to
35 recover about 6% to 12% of distillate; and continuing the reaction until at least about 85% of the aldehyde equivalents in the total quantity of glyoxal to be charged

for making the condensation product have reacted. The above temperature of phenol reaction with glyoxal, including the distillations, is 80° C to 100° C. After at least about 85% of the aldehyde equivalents have reacted as
5 discussed above, the temperature is raised and the reaction mixture is distilled at a temperature within the range of about 130° C to about 170° C to remove catalyst and water. Unreacted phenol remaining after removal of the catalyst is removed by distillation at temperatures above those used
10 for removal of the catalyst so that the free phenol in the polyphenol condensate is not more than about 5% and the reaction mixture is heated under vacuum at a temperature of about 175° to 200° C for about 0.25 to 3 hours to produce the phenol-glyoxal condensation product.

15

In a further aspect, this invention is directed to a method for preparing epoxy resins in the form of glycidyl ethers of the above described polyphenols by epoxidizing the polyphenol with a halohydrin in the presence of an
20 alkali metal hydroxide, e.g., sodium hydroxide.

In a still further aspect, this invention is directed to a method for preparing epoxy resins by reacting the phenol-glyoxal condensation product with a preformed epoxy
25 resin to prepare epoxy resin derivatives of the phenol-glyoxal condensation products.

In yet other aspects, this invention is directed to the polyphenols prepared by the methods of this invention
30 and epoxidized products prepared therefrom.

In yet further aspects, this invention is directed to compositions containing the phenol-glyoxal condensation products or epoxidized derivatives thereof and compositions
35 with other phenolic novolacs and/or epoxidized derivatives thereof.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 of the drawing is a graph showing fluorescence spectra of various epoxidized products. Letter "A" indicates the fluorescence spectra curve of EPON 1031 (CAS: 7328-97-4) which is a commercial epoxy resin of a polyphenol having less than 1% of free phenol which is commercially used for AOI fluorescence in the same wavelengths which are shown in the graph. EPON 1031 is sold by Shell Chemical Co. Letter "B" indicates the fluorescence spectra curve of the epoxidized product of Example 5A of this application wherein the epoxidized product is produced by the same method as shown in Example 8 herein. Letter "C" indicates the fluorescence spectra of the epoxide product of Example 8.

15

It can be seen from FIG. 1 of the drawing that the polyglycidyl ether of the phenol-glyoxal condensation product of this invention has unexpectedly greater fluorescence at an excitation wavelength 442 for an acquisition time of one second when measured within the range of 450 to 650 nm in comparison to the commercial product EPON 1031 as well as the polyglycidyl ether of the product of Example 5A.

25

DETAILED DESCRIPTION OF THE INVENTION

The Phenolic Monomer

The phenolic monomer, also referred to simply as a phenol, is a phenol which can be unsubstituted or substituted, e.g., with alkyl, phenyl or alkoxy groups. Typical phenolic monomers are the mononuclear or binuclear, monohydroxyphenols which have at least one ortho or para position available for bonding.

The phenolic monomer will typically contain up to about 12 carbon atoms and preferably up to about 8 carbon atoms. Such compounds include: phenol itself; alpha-naphthol; phenylphenol; cresols, e.g., 2-methylphenol and

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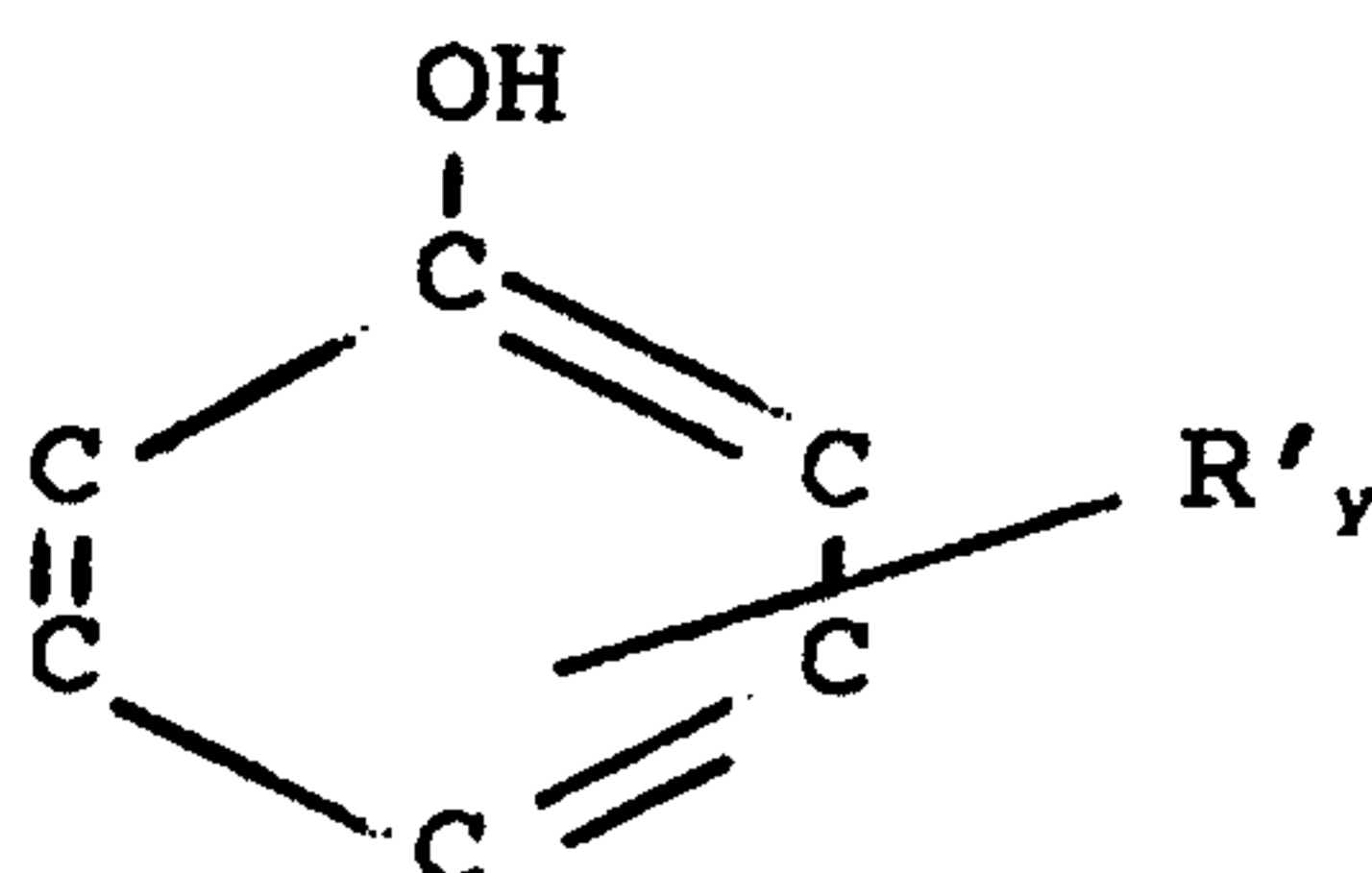
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3-methylphenol; various xylenols, e.g., 2,5-dimethylphenol and 3,5-dimethylphenol; and other alkyl phenols; and alkoxyphenols such as 2-methoxy- or 3-methoxyphenol. Mixtures of phenolic compounds can be used. A preferred phenolic compound is unsubstituted phenol, i.e., phenol itself.

Preferred phenolic monomers can be represented by the following formula:

10



15 wherein R' is selected from phenyl, alkyl of 1 to 4 carbon atoms and alkoxy of 1 to 4 carbon atoms and y is an integer of 0 to 3.

When R' is alkyl or alkoxy, y is 1 to 3, and when R' is phenyl, y is 1. Mixtures of the phenolic monomers can also
20 be used.

The Glyoxal Reactant

The glyoxal reactant can be in various forms such as relatively pure monomeric glyoxal, polymerized glyoxal or
25 glyoxal dissolved in water and mixtures thereof.

Illustratively, glyoxal is normally used as a 40% solution in water.

The Acid Catalyst

30 The acid catalyst is one which can be removed from the reaction mixture by distilling the reaction mixture at a temperature above about 80° C. but below about 170° C and preferably below about 160° C. Illustratively, the catalyst can be oxalic acid or a trihaloacetic acid or mixtures
35 thereof.

In the case of oxalic acid as catalyst, the

temperature of the reaction mixture is raised above about 130° C such as up to about 170° C together with distillation and preferably the temperature is raised to about 140° C to about 160° C so that the oxalic acid catalyst is decomposed to volatile components.

Oxalic acid can be used in its various forms such as the pure compound, the dihydrate, or mixtures thereof, all of which are referred to as oxalic acid herein.

10

Illustrative of the trihaloacetic acid catalyst there can be mentioned: trichloroacetic acid and trifluoroacetic acid. Trifluoroacetic acid may need to be replenished during the reaction since a portion thereof distills together with the water. Trifluoroacetic acid forms an azeotropic mixture in water. Therefore, when it is desired to remove the trifluoroacetic acid catalyst, it is preferred that a series of distillations be made with the addition of water after each distillation so as to remove substantially all of the acid.

When trichloroacetic acid is used as the catalyst, the temperature is raised up to about 170° C to remove the catalyst after any hydrochloric acid to be formed from the trichloroacetic acid is neutralized.

The quantity of the catalyst can vary from about 1% to about 6% based on the weight of the phenol charged to the reaction mixture. The quantity of oxalic acid is from about 1% to 6%, preferably about 1.5% to about 5% and particularly about 2.5% to about 4% based on the weight of phenol charged to the reaction mixture. When a trihaloacetic acid is used as catalyst, the quantity of catalyst is preferably from about 1% to about 4% by weight based on the phenol charged to the reaction mixture and particularly about 1% to about 3%. Mixtures of the acid catalysts can also be used.

The Reaction Conditions

The polyphenols (condensation products) of this invention may be prepared by continuous or step-wise contact of the glyoxal with a molar excess of the phenol in the presence of the acid catalyst. Illustratively, for stepwise reaction, a phenol and the acid catalyst are charged to a reactor and then an initial increment of the glyoxal is charged to the reactor while the reaction mixture is maintained at a temperature of about 80° C to about 100° C. The glyoxal reacts with the phenol and then additional glyoxal is charged to the reaction mixture.

The molar ratio of glyoxal to phenol in the manufacture of the phenol-glyoxal condensation products is from about 0.15 to 0.22 moles of glyoxal for each mole of phenol charged and preferably about 0.16 to 0.20 moles of glyoxal for each mole of phenol charged. When a total of two increments of glyoxal are made to the reaction mixture, it is preferred that each increment be from about 0.06 to 0.11 moles of glyoxal based on the total moles of phenol charged and particularly about 2 equal molar quantities of the glyoxal. Total mole ratios of less than about 0.15 moles of glyoxal for each mole of phenol charged give more of the tetraphenols, such as TPE which is essentially devoid of optical properties in the ranges given above for AOI quality control. Ratios of greater than about 0.22 moles of glyoxal for each mole of phenol lead to longer reaction times and are likely to give product with higher viscosity.

30

The aldehyde equivalents or aldehyde units in the reaction mixture are maintained at less than about 70%, and preferably less than about 60% of the total aldehyde equivalents or aldehyde units which will be charged to the reaction mixture for making the phenol-glyoxal condensate. Thus, not more than about 70% of the aldehyde equivalents to be used in the reaction are present in the reaction

mixture at any one time.

The catalyst is removed from the reaction mixture after at least about 85% of the aldehyde equivalents of the total aldehyde equivalents to be charged to the reactor have reacted, and preferably when from about 90% to 95% of such aldehyde equivalents have reacted. Then the temperature is generally raised to remove the catalyst. However, when trichloroacetic acid is the catalyst, a basic material is added to the reaction mixture in an amount sufficient to neutralize any hydrochloric acid to be formed as a decomposition product of such acid before distillation is effected to remove the catalyst.

When the basic material used to neutralize hydrochloric acid is an alkali metal oxide or hydroxide or an alkaline earth metal oxide or hydroxide, e.g., sodium hydroxide or calcium hydroxide about 80% molar equivalents of such base are added based on the molar equivalents of the trichloroacetic acid used as catalyst. When an amine is used as the basic material, about 10% to 20% of the amine molar equivalents are added to the reaction mixture for neutralizing HCl based on the molar equivalents of trichloroacetic acid used as catalyst. It is preferred that the basic material be an amine so that metal ions such as that of alkali metal or alkaline earth metals not be included in the product. The presence of metal ions is deleterious for use of the product in the more demanding electronic applications. Illustrative of amines for neutralizing the hydrochloric acid there can be mentioned amines having a pKa value of about 5 to about 11 such as pyridine, picoline, benzyldimethylamine, triethylamine, and hydroxyethyldiethylamine.

The total time for the condensation reaction of aldehyde with the phenol will typically vary from about 5 to about 15 hours and preferably about 8 to 12 hours.

The temperature of the condensation reaction of the phenol and glyoxal in the presence of the catalyst, including distillations, will be in the range of from about 80° C to about 100° C and preferably from about 85° C to 95° C. until at least about 85% or more of the aldehyde equivalents in the total quantity of glyoxal to be charged for making the condensation product have reacted.

Water is removed continuously or intermittently by distillation, such as after the reaction of glyoxal with phenol following individual additions of the glyoxal, since accumulation of water in the reaction mixture slows the reaction. Water is formed by the condensation reaction of glyoxal with phenol and additionally water is generally present in the glyoxal charge, e.g., glyoxal is generally used as a 40% solution in water.

The water content in the reaction mixture is preferably kept to below about 8% by weight based on the phenol charged to the reaction mixture and preferably below about 6% based on the weight of phenol charged to the reaction mixture. Illustratively, two or more, e.g. 2 to 4, additions of the glyoxal are made to the reaction mixture with distillation of water after reaction of glyoxal with the excess phenol. Preferably, an initial glyoxal charge is made with the subsequent reaction followed by distillation of water and then a second glyoxal charge is made followed by reaction of the monomers prior to reacting at least about 85% of the total aldehyde equivalents to be used for making the condensation product.

Instead of monitoring the progress of the reaction by measuring aldehyde equivalents, the time of reaction can be used for conducting the reaction when the reactants and catalysts are the same and the operating conditions are within the same ranges, e.g., mole ratios, reaction

temperatures, the catalyst and the quantity thereof; times for distillation of water and the amount of distillate. Illustratively, the following steps and time periods can be used when: total molar ratio of glyoxal to phenol is from about 0.15 to 0.22; a 40% solution of glyoxal is reacted with phenol itself at a temperature of 80° C to 100° C; an initial glyoxal charge is made with subsequent reaction of the glyoxal with phenol and in time by distillation, followed by another glyoxal addition followed by continued reaction and then distillation which is followed by continued reaction before depletion of the aldehyde equivalents to 15% or less of that charged. From about 0.06 to 0.11 moles of the glyoxal, based on the amount of phenol charged, are added with each charge of the glyoxal. Thus, after addition of the initial quantity of glyoxal, the aldehyde is reacted with the phenol for about 1 to 5 hours, preferably 1.5 to 3 hours and then there is distilled from about 8% to 12% of a first distillate from the reaction mixture based on the weight of phenol charged.

After the first distillation, which is also conducted within the temperature range of about 80 to 100° C another 0.06 to 0.11 moles of glyoxal based on the moles of phenol charged, are slowly added to the reaction mixture. Preferably, there is charged about equal quantities of glyoxal during each addition. Heating of the reaction mixture is continued for another 1 to 6, preferably 1.5 to 5 hours from the time the first distillation commenced and then a second distillation is started to remove about another 4% to 12% of water based on the phenol charged. After the second distillation, the reaction is permitted to continue for another 0.5 to 6, preferably 1 to 4 hours from the time the second distillation commenced before the temperature is raised for distillation together with removal of the catalyst.

35

The temperature of 80° C to 100° C is used until it is time to raise the temperature and remove the catalyst or

unreacted phenol. Such distillation, prior to increasing the temperature for removal of catalyst, is conducted under vacuum so as to assist in the control of the temperature. The vacuum can vary from about 15 to 25 inches or more of 5 mercury.

The temperature for removal of the catalyst by distillation is less than about 170° C, preferably less than about 160° C. When oxalic acid is the catalyst, the 10 temperature is raised above 135° C to about 170° C, particularly about 155° C to about 160° C.

All or some of the water is removed at the time the catalyst is removed. In the case where oxalic acid is the 15 catalyst, all or substantially all of the water is removed when the catalyst is removed from the reaction mixture. Any water remaining in the reaction mixture after elimination of the catalyst is finally removed by the distillation in removal of the phenol.

20

After removal of the water and all of the catalyst, unreacted (free) phenol is removed from the reaction mixture so as to bring the free phenol content of the reaction mixture to less than about 5%, preferably to less 25 than about 2% and particularly less than about 1.5% by weight of the reaction mixture.

Removal of the unreacted phenol is attained by conventional means such as in the removal of unreacted 30 phenol in novolac resins, e.g., flash distillation by heating the reaction mixture at an elevated temperature under vacuum. Thus, the temperature can be up to about 190° C or 200° C under about 25 to 30 inches of mercury. Steam sparging under vacuum at such temperatures can also be used 35 to remove phenol in the product.

Concurrently with removal of phenol or as a separate

step following removal of the catalyst, the reaction mixture is heated at a temperature of from about 175° C to about 200° C and preferably from about 180° C to about 195° C. Such heating is conducted for a period of about 0.25 to 3 hours and preferably for about 0.5 to 2 hours. All or a portion of such heating can be conducted at the time the phenol is removed under vacuum. Optionally, the phenol-glyoxal condensation product with 5% or less of unreacted phenol can be placed in an inert atmosphere and heated to conduct a portion or all of the heating in the range of about 175° C to 200° C for about 0.5 to 3 hours. Illustrative of an inert atmosphere there can be mentioned nitrogen or argon. After such heating step at about 175° C to 200° C and reduction of phenol in the reaction mixture to less than 5%, the reaction mixture is also referred to as the phenol-glyoxal condensation product.

The phenol-glyoxal condensation product is eventually cooled and generally comminuted, e.g., flaked.

Preparation of Polyepoxides

Epoxidized products of this invention can be prepared by at least two different conventional routes. One route is by reaction of the phenol-glyoxal condensate product with a halohydrin in the presence of an alkali metal hydroxide to form glycidyl ethers of the polyphenol. Such epoxidized products will typically have epoxy equivalents of about 190 to 230 and preferably about 205 to 225. The other route is by reacting a molar excess of a preformed polyfunctional epoxide with the phenol-glyoxal condensation product. Such epoxidized products by the other route will typically have epoxy equivalents of about 140 to 250 and preferably about 160 to 230.

In the first route, the polyepoxide is prepared by

contacting the phenol-glyoxal condensation product with an excess of epichlorohydrin in the presence of an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide at a temperature within the range of about 50° C to about 80° C. Optional catalysts, such as quaternary ammonium salts, may be employed. The reaction can be carried out in the presence of an inert solvent, including alcohols such as ethanol, isopropanol, methyl isobutyl ketone (MIBK), toluene, ethers, and mixtures thereof.

10

Another method for preparing the polyepoxide by the first route is set forth in U.S. 4,518,762 of May 21, 1985 to Ciba Geigy Corp. which is incorporated herein by reference in its entirety. Briefly, in this process, the polyphenol, preferably the phenol-glyoxal purified product, is reacted at a temperature of 40° to 100° C, in the absence of any catalyst specific for the formation of the chlorohydrin ether intermediate, in the presence of 2 to 25% by weight, based on the reaction mixture, of a lower alkanol or lower alkoxyalkanol cosolvent, with excess epichlorohydrin, based on the phenolic hydroxy value, in the presence of 0.5 to 8% by weight of water, based on the reaction mixture, and with 0.9 to 1.15 equivalents of solid alkali metal hydroxide per phenolic hydroxyl group to give the epoxy derivative of the polyphenol and wherein there is 0.5% to 8 % by weight of water in the reaction mixture throughout the reaction period, using a solid alkali metal hydroxide in the form of beads of about 1 mm diameter, which hydroxide is charged to the reaction mixture portionwise or continuously during a gradually escalating addition program, and then isolating the epoxy novolac resin.

In the second route for preparation of the epoxy resins containing the phenol-glyoxal condensation products of this invention, one part by weight of such condensation product is reacted with 4 to 8 parts of a polyepoxide at

about 100° C to about 150° C using a catalyst, e.g., potassium hydroxide, benzyldimethylamine, benzyltrimethylammonium hydroxide, 2-methyl imidazole, and 2,4,6-tris(dimethylaminomethyl)phenol. Typical catalyst levels are about 0.1% to about 0.6% based on the reaction mass. Typical polyepoxides for reaction with the phenol-glyoxal condensation product are those of diglycidyl ether resins, e.g., the diglycidyl ether resins of: bisphenol A; bisphenol F; resorcinol; neopentyl glycol; cyclohexane dimethanol; and mixtures thereof.

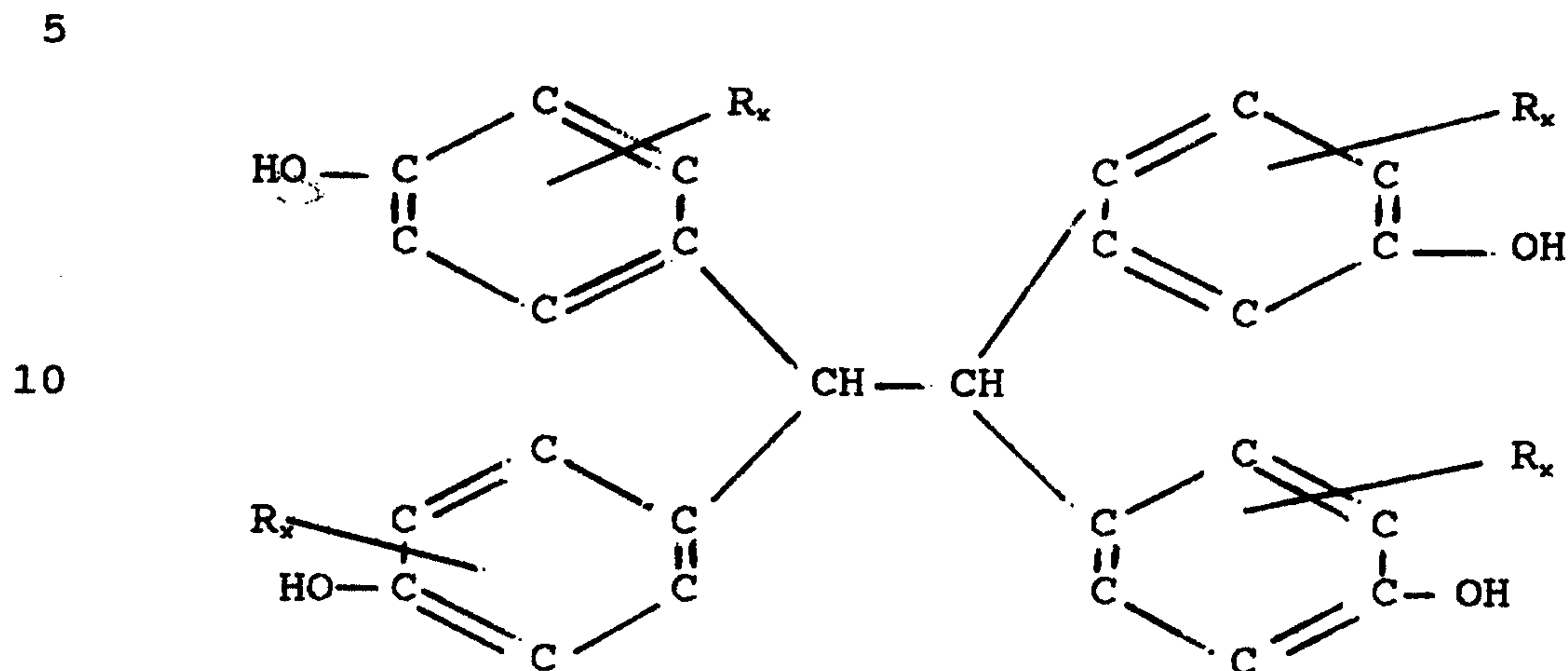
The phenol-glyoxal condensation products of this invention can also be partially epoxidized without sacrifice in the desirable optical properties by reduction of the quantity of alkali used in the reaction with epichlorohydrin. Illustratively, reduction of caustic to about 40% to 70% of that in the methods of the above described first route affords partially epoxidized derivatives.

The Phenol-Glyoxal Condensation Products

Properties of the phenol-glyoxal condensation products are as follows:

<u>Property</u>	<u>Broad Range</u>	<u>Preferred Range</u>
Mw/Mn	400-600/300-390	440-540/320-370
Viscosity,		
25 cps at 175° C	300-2500	450-1500
Free Phenol (%)	0-5	0.03-1.5
Tetraphenol ethane		
such as TPE (%)	0-6	1-4
UV absorbance at		
30 350 nm	at least 0.400	at least 0.450 particularly >0.5
UV absorbance at		
365 nm	at least 0.260	at least 0.275 particularly >0.30
35		

The phenol-glyoxal condensation products contain a variety of compounds, including polyphenols such as di-, tri-, and tetraphenols. Illustratively, such tetraphenols can be represented by the formula:



wherein x is an integer of 0 to 3. When R is alkyl and or alkoxy x is 1-3 and the alkyl and alkoxy groups have 1 to 4 carbon atoms. When the reactants are phenol itself and glyoxal, the above polyphenol is tetrakis(4-hydroxyphenyl)ethane (TPE) which is also referred to as 1, 1, 2, 2-tetrakis(4-hydroxyphenyl)ethane. Epoxidation of the tetrakis(4-hydroxyphenyl)ethane gives the tetraglycidyl ether of tetrakis(4-hydroxyphenyl)ethane.

25 Unless trichloroacetic acid is used as catalyst with metal ion oxides or hydroxides for neutralization of the hydrochloric acid, the phenol-glyoxal condensation products of this invention will typically have a percent by weight concentration of metal ions of less than about:

30 0.005% for sodium; 0.003% for calcium; 0.003% for iron; and 0.002 % for potassium.

The polyepoxide products of this invention when used in electronic applications such as laminates for the production of printed circuit boards will typically

35 comprise the following composition based on 100 parts of a conventional epoxy resin, e.g., an epoxy resin such as the

diglycidyl ether of bisphenol A: (a) about 18-25 parts of phenol-formaldehyde novolac;

- (b) about 3-10 parts of a member selected from the group consisting of a glycidylated phenol-glyoxal
5 condensation product, a reaction product of an epoxy resin and a phenol-glyoxal condensation product, a phenol-glyoxal condensation product and mixtures thereof; and
(c) optionally, an epoxy curing accelerator.

- 10 The conventional epoxy resin making up the 100 parts of the composition is preferably a flame retardant epoxy resin such as a halogenated epoxy resin, e.g., chlorinated or brominated epoxy resin. Illustrative of such brominated
15 epoxy resins there can be mentioned the brominated product of the diglycidyl ether of bisphenol A, e.g., EPON 1124 (CAS: 26265-08-07) of Shell Chemical Co. This brominated epoxy resin can be used in flame retardant compositions with epoxy resins such as those of glycidyl ethers of a phenolic/ novolac, glycidyl ethers of an o-
20 cresol/formaldehyde novolac, diglycidyl ethers of bisphenol A, diglycidyl ethers of bisphenol F, diglycidyl ethers of resorcinol, diglycidyl ethers of neopentyl glycol or diglycidyl ethers of cyclohexanedimethanol and mixtures thereof. Epoxy curing accelerators are used in a quantity
25 sufficient to accelerate the cure of the epoxy resin. Generally, such quantity is from about 0.05 to 0.5 parts based on 100 parts of the base epoxy resin and particularly about 0.1 to 0.2 parts. Such accelerators include 2-methylimidazole, 2-ethyl-4-methylimidazole, amines such as
30 2,4,6-tris (dimethylaminomethyl)phenol and benzyldimethylamine, and organophosphorus compounds such as tributylphosphine and triphenylphosphine.

- The phenol-glyoxal condensation products of this
35 invention in mixtures with other phenol-novolacs having UV absorbance of less than 0.260 at 365 nm, have utility as curing agents for epoxy resins. Such other phenolic

novolacs can comprise from about 50% to 90% of such curing composition and the phenol-glyoxal condensation product can comprise 10 to 50% of such curing composition. About 15 to 30 parts of this type of curing composition can be used to cure 100 parts of epoxy resin. Illustrative of such other novolacs, there can be mentioned those prepared from formaldehyde and phenol or a substituted phenol as well as mixtures thereof; those prepared from bisphenol A and naphthol as well as such polycyclic phenols which are substituted. Substituents for the monomers include hydroxy, alkyl of 1 to 4 carbon atoms, alkoxy of 1 to 4 carbon atoms as well as phenyl. Preferred resins of the other novolacs include phenol-formaldehyde novolacs and ortho-cresol-formaldehyde novolacs having a molecular weight of 1,000 to 5,000.

The weight average molecular weight (Mw) and number average molecular weight (Mn) herein are measured using gel permeation chromatography and phenolic compounds and polystyrene standards. The sample molecular weight to be measured is prepared as follows: the sample is dissolved in tetrahydrofuran and the solution is run through a gel permeation chromatograph. Any free phenol in the sample is excluded from calculation of molecular weight.

The quantity of TPE in the various reaction mixtures was determined by the following method.

(a) The reagents used were para-ethyl phenol, TPE, and silylation reagent.

(b) Procedure for determining TPE was as follows: A silylation reagent was prepared as follows: into 25 ml (milliliter) reaction flask, add by syringe: 10 cc (cubic centimeters) of pyridine, 3 cc of trimethylchlorosilane (TMCS), and 10 cc of hexamethyldisilazane (HMDS). This was left to stand for 5 to 10 minutes.

(c) The TPE standard solution is prepared as follows: Weigh into vial (appropriate for silylation) approximately

30 mg each TPE and p-ethylphenol. Add 1 cc silylation reagent. Shake until dissolved (approximately 10 minutes). Heat in low temperature oven overnight. Inject 1 microliter into gas chromatograph. Use methyl ethyl ketone as rinses.

5 The column used for this analysis is Dexsil 300 which is supplied by Supelco of Belfonte, Pa.

In order that those skilled in the art may more fully understand the invention presented herein, the following

10 examples are set forth. All parts and percentages in the examples, as well as elsewhere in this application are by weight, unless otherwise specifically stated.

The following examples are illustrative of the

15 invention. Some of the examples are designated as "comparative" to show differences from examples which are part of this invention and not necessarily as comparisons with the prior art.

20

EXAMPLE 1

PREPARATION OF PHENOL-GLYOXAL CONDENSATION PRODUCT
AT 90° C WITH TWO ADDITIONS OF GLYOXAL

To 1,728 grams (g) (18.36 moles) phenol and 69.1 g

25 oxalic acid dihydrate at 90° C there was added over 30 minutes 227 g of 40% glyoxal in water (1.57 moles). The temperature was maintained at 90° C for another 1.5 hours and then there was vacuum distilled 185 g of distillate (10.7% based on the weight of phenol charged) from the

30 reaction mixture at 90° C over a period of forty minutes. After such heating, approximately 79% of the aldehyde equivalents charged until that time had reacted and the quantity of water in the reaction mixture was about 4%. Another 227 g of 40% glyoxal in water (1.57 moles) was

35 added to the reaction mixture over a 25 minute period while the temperature was maintained at 90° C for 1.5 hours and then there was vacuum distilled 195 g of distillate (11.3%

based on the weight of phenol charged) at 90° C over a period of thirty minutes. After such heating approximately 70% of the aldehyde equivalents charged until that time had reacted and the water content of the reaction mixture was about 3.5%. The molar ratio of glyoxal to phenol for the total of both glyoxal additions was 0.17. The temperature of 90° C was maintained for another 1.5 hours. After such heating, 90% of the aldehyde equivalents charged to the reaction mixture until that time had reacted and the water content was about 4.5%. Then the reaction mixture was distilled at atmospheric pressure to 160° C and held at 160° C for one hour. The reaction mixture was then vacuum distilled to remove the bulk of unreacted phenol at 155-160° C. Vacuum distillation was continued up to a temperature of 190° C and held at that temperature for one hour until phenol in the reaction mixture was less than 1%. The resulting phenol-glyoxal condensation product was then comminuted, e.g., flaked. During the reaction the aldehyde equivalents in the reaction mixture were maintained at less than about 70% of the aldehyde equivalents in the total quantity of glyoxal to be charged for making the phenol-glyoxal condensation product. Properties of the phenol-glyoxal condensation product are given in tables which follow.

In the tables which follow, this example is also referred to as EX1.

EXAMPLE 2 (COMPARATIVE)

PREPARATION OF PHENOL-GLYOXAL POLYPHENOL AT 90° C WITH ONE ADDITION OF GLYOXAL

To 576 g (6.12 moles) phenol and 23 g oxalic acid dihydrate at 85° C is added over a period of about one hour 151.4 g of 40% glyoxal in water (1.04 moles) during which period the temperature was slowly raised to 90° C. The mole ratio of glyoxal to phenol was 0.17. Immediately thereafter, vacuum is applied to remove 120 g of distillate at 90-95° C over a period of 60 minutes. A temperature of 90-92° C was maintained for 2.25 hours after which time

about 82% of the aldehyde equivalents charged had reacted. Then vacuum was applied over 15 minutes to remove 13.3 g of distillate. Heating was continued at 90° C to 91° C for 1.25 hours. After the 1.25 hour period approximately 88% of
5 aldehyde equivalents charged had reacted. Vacuum was then applied over 6 minutes to remove 6.68 g of distillate. Heating at 90° C was continued for 5 hours and one hour at 100° C. After such heating for one hour, about 94% of the aldehyde equivalents charged to the reaction mixture had
10 reacted. The reaction mixture was atmospherically distilled to 160° C. The temperature of 160° C was held for one hour. The reaction mixture was then vacuum distilled to remove the bulk of unreacted phenol at 155-160° C and the vacuum distillation was continued at 190° C until
15 phenol in the reaction mixture was less than 1%. During the vacuum distillation the reaction mixture was heated at a temperature of about 175° C to 192° C for about 0.25 hours. The reaction mixture is then discharged from the reactor and then comminuted, e.g., flaked. Properties of the
20 polyphenol product of this example are given in tables which follow and this example may be referred to as EX2.

EXAMPLE 3 (COMPARATIVE)

PREPARATION OF PHENOL-GLYOXAL POLYPHENOL AT 102° C AND
25 REFLUX (103-104° C) WITH ONE ADDITION OF GLYOXAL

To 576 g (6.12 moles) phenol and 23 g oxalic acid dihydrate at 90° C there was added over a one hour period 151.4 g of 40% glyoxal in water (1.04 moles) while the temperature was allowed to rise to reflux (103-104° C). The
30 mole ratio of glyoxal to phenol was 0.17. The reaction mixture was held at reflux for 10 hours. After such reflux approximately 89% of the aldehyde equivalents had reacted. The temperature was then raised to 110° C and there was removed 55.5 g of distillate over a period of about 22
35 minutes. The temperature was held at 110° C for one hour and then the reaction mixture was atmospherically distilled to 160° C. The reaction mixture was then held for one hour

at 160° C. The reaction mixture was then vacuum distilled to remove the bulk of unreacted phenol at 155-160° C and the vacuum distillation was then continued at 176° C until phenol in the reaction mixture was less than 3%. During the reaction, the aldehyde equivalents in the reaction mixture were maintained at less than about 70% of the aldehyde equivalents in the total quantity of glyoxal to be charged for making the condensation product. The reaction mixture was then discharged from the reactor and comminuted, e.g., flaked. Properties of the polyphenol product of this example are given in tables which follow and this example may be referred to as EX3.

EXAMPLE 4 (COMPARATIVE)

PREPARATION OF PHENOL-GLYOXAL POLYPHENOL AT 102° AND REFLUX (103-104° C) WITH ONE ADDITION OF GLYOXAL

To 576 g (6.12 moles) phenol and 6.23 g 18.5% HCl (0.2% HCl on phenol) at 90° C is added over a one hour period 151.4 g of 40% glyoxal in water (1.04 moles) while the temperature is allowed to rise to reflux (103-104° C). The molar ratio of glyoxal to phenol was 0.17. After two hours at reflux about 93% of the aldehyde equivalents charged had reacted. The reaction mixture was then vacuum distilled with the temperature rising to 110° C to remove aqueous HCl distillate of 116.4 g. 100 g of hot water was then added to the reaction mixture and distillation was continued at atmospheric pressure to 150° C. The hydrochloric acid catalyst (HCl) is co-distilled with water from the reaction mixture. Then, by vacuum distillation up to 180°, the unreacted phenol was removed to less than 4% remaining in the reaction mixture. The reaction mixture is then discharged from the reactor and comminuted, e.g., flaked. Properties of the polyphenol product of this example are given in the tables which follow and this example may be referred to as EX4.

EXAMPLE 5 (COMPARATIVE)

PREPARATION OF PHENOL-GLYOXAL POLYPHENOL AT 102° C AND REFLUX (103-104° C) WITH ONE ADDITION OF GLYOXAL AND PHENOLSULFONIC ACID CATALYST

5 To 576 g (6.12 moles) phenol and 5.76 g (grams) (1.5% based on phenol) of 65% phenolsulfonic acid at 90° C as catalyst there is added over a one hour period 151.4 g of 40% glyoxal in water (1.04 moles). The mole ratio of glyoxal to phenol is 0.17. The temperature of the reaction
10 mixture is permitted to rise to reflux (103-104° C) where it remained for several hours and the conversion of aldehyde equivalents was up to about 96% of that charged. This is followed by neutralization of the catalyst, cooling to 65° C and washing with distilled water to remove salt.
15 This is followed by atmospheric distillation to 160° C and then vacuum distillation at about 176° C to reduce the quantity of unreacted phenol in the reaction mixture to about 1%. The reaction mixture is eventually comminuted, e.g., flaked.

20

EXAMPLE 5A (COMPARATIVE)

The procedure of the above Example 5 was followed but the phenolsulfonic acid was replaced by 1.25 g (0.22% based on phenol) of anhydrous methanesulfonic acid. Approximately
25 97% of the aldehyde equivalents charged had reacted prior to neutralization of the catalyst. Essentially, equivalent properties, molecular weights, viscosities, and % of TPE is obtained. Properties of the phenol-glyoxal condensation product are given in tables which follow wherein this
30 example may be referred to as EX5A.

EXAMPLE 6

LARGE SCALE PRODUCTION OF PHENOL-GLYOXAL CONDENSATION PRODUCT IN THE MANNER OF EXAMPLE 1

35 The phenol-glyoxal condensation product of Example 6 was prepared in substantially the same manner as Example 1 except that it was prepared on large scale equipment which

can produce several hundred pounds of product and was vacuum steam sparged at 190° C to reduce phenol below 0.1%. The percent insolubles were 0.04% for the phenol-glyoxal condensation product of this example whereas other
5 properties are given in tables which follow wherein this example may be referred to as EX6. The test for insolubles was conducted by essentially dissolving 15 g (grams) of condensate in 285 mls (milliliters) of isopropanol, filtering through a No. 42 Whatman filter paper and then
10 drying the paper in an oven at 75° C to 100° C for 30 minutes.

EXAMPLE 7.

LARGE SCALE PRODUCTION OF PHENOL-GLYOXAL CONDENSATION PRODUCT IN THE MANNER OF EXAMPLE 1

15

The phenol-glyoxal condensation product of Example 7 was prepared in the same manner as that of Example 6, except that it was prepared at a different time. The percent insolubles in the product were 0.01% whereas other
20 properties are given in tables which follow wherein this example may be referred to as EX7. The test for insolubles was performed in the same manner as in Example 6 above.

EXAMPLE 8

25 PREPARATION OF POLYGLYCIDYL ETHER RESIN (EPOXY RESIN)

A one liter flask was charged with: 75 g (grams) of the flaked reaction product of Example 6; 200 g of isopropyl alcohol; and 52.5 g of water to form a reaction mixture. The reaction mixture was heated to 55° C. After 10
30 minutes there was add 388.5 g of epichlorohydrin. The reaction mixture was reheated to 55° C and then 30 g of a 20% solution of sodium hydroxide in water was added while maintaining a temperature of 55° C. The 55° C temperature was held for another 30 minutes. Then there was added 90 g
35 of 20% solution of sodium hydroxide in water. The reaction mixture was held at 55° C for another hour, heated to 65° C and held for 30 minutes and then transferred to a

separatory funnel. The upper clear brown organic layer (145.6 g) was stirred with 150 g water and 50 g of dry ice. The aqueous layer was discarded and the organic layer washed a second time and then vacuum distilled to recover
5 excess epichlorohydrin and 105 g of dark resin of the epoxidized product of Example 6. This epoxy resin has a weight per epoxy equivalent of 203.1 and 225.8. This compares with a weight per epoxy equivalent of 210 for EPON 1031. Viscosities and weight per epoxy equivalent (WPE) of
10 the epoxy resin of this Example 8 as well as comparisons with other epoxy resins prepared from polyphenols are shown below in tables wherein this example may be referred to as EX8.

15

EXAMPLE 9 (COMPARATIVE)

PREPARATION OF PHENOL-GLYOXAL POLYPHENOL USING ACIDIC (SULFONIC ACID) ION EXCHANGE RESIN

To 709.3 g of phenol (7.54 moles) and 35.5 g of
20 Amberlyst 15 which is a dry sulfonic acid ion exchange resin sold by Rohm & Haas Co. at a temperature of 90° C over 30 minutes, there was added 93 g of 40% glyoxal in water (0.64 moles). This resin was chosen since the resin used as catalyst in U.S. patents: 5,012,016; 5,146,006; and
25 5,191,128, all to S. Li, were unavailable and this resin appeared to be the closest to such resin. The temperature was maintained at 90° C for another 1.5 hours. After such time 88% of the aldehyde equivalents charged to the reaction mixture had reacted. Then there was vacuum
30 distilled 42 g of distillate. On completion of the distillation 95% of the aldehyde equivalents charged to the reaction mixture had reacted. Another 93 g of 40% glyoxal in water was added over 31 minutes while the temperature was maintained at 90° C for 1.5 hours. After such 1.5 hours,
35 81% of the aldehyde equivalents charged to the reaction mixture had reacted. Then there was vacuum distilled 70 g of distillate at 90° C over a period of 30 minutes. The

temperature of 90° C was maintained for another 30 minutes after which time, 91% of the aldehyde equivalents charged to the reaction mixture had reacted. The molar ratio of glyoxal to phenol for the total of both glyoxal additions was 0.17. Catalyst was allowed to settle and relatively clear liquor (687 g) decanted off and neutralized to pH of 6 with 2.6 g of 50% sodium hydroxide. 650 g of neutralized solution was charged to a flask for atmospheric distillation to 160° C. The reaction mixture was then vacuum distilled to 175° C to remove phenol. During the reaction, the aldehyde equivalents in the reaction mixture were maintained at less than about 70% of the aldehyde equivalents in the total quantity of glyoxal to be charged for making the polyphenol. Yield of product was 263 g. The resulting polyphenol was then comminuted, e.g., flaked. Properties of the polyphenol are given in tables which follow wherein this example may be referred to as EX9.

EXAMPLE 10

20 PREPARATION OF PHENOL-GLYOXAL CONDENSATION PRODUCT WITH TWO ADDITIONS OF GLYOXAL, OXALIC ACID CATALYST AND TOTAL GLYOXAL/PHENOL MOLE RATIO OF 0.22 FOR FIRST PORTION AND ADDITION OF PHENOL TO REDUCE THE GLYOXAL/PHENOL MOLE RATIO TO 0.17 FOR SECOND PORTION.

25

To 1419 g (15 moles) phenol and 56.5 g oxalic acid dihydrate at 90° C there was added over 30 minutes 240 g of 40% glyoxal in water (1.655 moles). The temperature was maintained at 90° C for another 1.5 hours and then there was vacuum distilled 148.3 g of distillate from the reaction mixture at 90° C over a period of fifty minutes whereupon about 62% of the aldehyde equivalents charged to the reaction mixture had reacted after such fifty minute period. Another 240 g of 40% glyoxal in water (1.655 moles) was added to the reaction mixture over a 22 minute period while the temperature was maintained at 90° C for 1.5 hours. About 58% of the aldehyde equivalents charged to

the reaction mixture had reacted after this 1.5 hour period. There was then vacuum distilled 212.2 g of distillate at 90° C over a period of 45 minutes. After such 45 minute period about 65% of the aldehyde equivalents

5 charged to the reaction mixture had reacted. The molar ratio of glyoxal to phenol for the total of all the glyoxal additions was 0.22. The temperature of 90° C was maintained for another 5 hours. After such 5 hour period about 87% of the aldehyde equivalents charged to the reaction mixture

10 had reacted. Then the reaction mixture was divided into two. To one half (794 g) was added 214 g of phenol to adjust glyoxal/phenol mole ratio to 0.17. The reaction mixture with added phenol was heated at 90° C for 2.5 hours whereupon 89% of the aldehyde equivalents charged to the

15 reaction mixture had reacted. Percent water in the reaction mixture was 4.9%. The reaction mixture was then heated to 160° C over 25 minutes and held at 160° C for one hour, after which the bulk of phenol was removed by vacuum distillation to 175° C. The product was then discharged from

20 the flask. The remaining one-half of reaction mixture without added phenol was heated to 160° C as above and phenol removed by vacuum distillation to 175° C. The phenol-glyoxal condensation product made with the 0.22 mole ratio of glyoxal to phenol is referred to in the tables as

25 EX10.22 whereas that made with the 0.17 mole ratio of glyoxal to phenol is referred to in the tables as EX10.17 During the reaction, for both EX10.17 and EX10.22, the aldehyde equivalents in the reaction mixture were maintained at less than about 70% of the aldehyde

30 equivalents in the total quantity of glyoxal to be charged for making the phenol-glyoxal condensation product. Properties of the polyphenols are given in tables which follow. The polyphenol of EX10.17 and that of EX10.12 were further heated at 190° C for one hour under full vacuum.

35 Properties of these products are shown in the following tables wherein the heated sample of EX10.17 is referred to as EX10.17H and that of EX10.22 is referred to as EX10.22H.

It can be seen from the tables that the heated samples show improved optical properties.

Example 11

5 PREPARATION OF PHENOL-GLYOXAL CONDENSATION PRODUCT WITH TWO ADDITIONS OF GLYOXAL, GLYOXAL-PHENOL MOLE RATIO OF 0.17 WITH TRICHLOROACETIC ACID CATALYST AND USE OF BASIC MATERIAL IN REMOVAL OF HCL.

10 To 709.3 g (7.54 moles) phenol and 17.7 g trichloroacetic acid (2.5% based on the weight of phenol charged) at 90° C there was added over 27 minutes 92.9 g of 40% glyoxal (0.64 moles) in water. The temperature was maintained for 1.5 hours and about 58% of aldehyde
15 equivalents had reacted after such 1.5 hours. Subsequently, there was vacuum distilled 62.2 g of distillate from the reaction mixture at 90° C over 26 minutes. After distillation, the aldehyde equivalents reacted (converted) was 70% of that charged and residual
20 water content of the reaction mixture was about 3.5% Another 92.9 g of 40% glyoxal (0.64 moles for a total of 1.28 moles) was added over half an hour while the temperature was maintained for 1.5 hours. The total mole ratio of glyoxal to phenol in this example was 0.17. After
25 such heating about 62% of aldehyde equivalents charged to the reaction mixture had reacted. Subsequently there was vacuum distilled 81.6 g of distillate at 90° C over 25 minutes. After the distillation, the aldehyde equivalents converted was 72% of that charged and the residual water in
30 the reaction mixture was 3.5%. The temperature was maintained at 90° C for another 1.5 hours and about 88% of the aldehyde equivalents charged had reacted after such 1.5 hour period. One half hour later 1.0 g of pyridine was added. At such time 88 percent of aldehyde equivalents
35 which had been charged to the reaction mixture had reacted. The temperature was raised to 125° C over one half hour and held at this temperature for 70 minutes and further raised

to 160° C for 1.5 hours and held at this temperature for 23 minutes to complete decomposition of acid. The phenol-glyoxal condensation product was further heated at 190° C for one hour under full vacuum to remove unreacted phenol and prepare the phenol-glyoxal condensation product which is also referred to as EX11 in the following tables.

During the reaction, the aldehyde equivalents in the reaction mixture were maintained at less than about 70% of the aldehyde equivalents in the total quantity of glyoxal to be charged for making the phenol-glyoxal condensation product.

EXAMPLE 12 (COMPARATIVE)

PREPARATION OF PHENOL-GLYOXAL CONDENSATION PRODUCT WITH TWO ADDITIONS OF GLYOXAL, GLYOXAL-PHENOL MOLE RATIO OF 0.17 WITH TRICHLOROACETIC ACID CATALYST WITHOUT USE OF BASIC MATERIAL IN REMOVAL OF HCL.

The procedure of Example 11 was followed except that: a basic material, e.g., pyridine, was not added to the reaction mixture prior to raising the temperature to 125° C and removal of the catalyst; and the final temperature after removal of phenol was 175° C. Processing of this example was discontinued upon heating to 175° C because the viscosity was unduly high. This example is also referred to in the tables as EX12.

TABLE 1

CHARACTERIZATION OF SOME PHENOL-GLYOXAL POLYPHENOLS

EX	Mol Wgt Mw/Mn	Phenol, %	TPE, %	Viscosity cps(175°C)
1	451/331	0.15	4.15	480
2	464/347 (465/362) ^(a)	0.29	5.10	510
3	468/351	2.05	8.53	300*
4	572/387	3.46	13.21	900*

	5A	538/376	1.13	10.1	891
	6	494/353	0.04	1.73	530
	7	508/358	0.04	2.74	670
	9	475/356	0.19	10.42	2,400
5	10.17	485/348	3.80	5.5	350*
	10.17H	496/357	<0.05	5.79	1088
	10.22	518/364	3.88	5.60	400*
	10.22H	528/366	<0.05	4.83	1700
	11	518/363	0.3	4.85	2040
10	12	552/357	0.30	1.02	> 9,000

(a) value before catalyst was removed.

* These examples have a high phenol content which depresses the viscosity.

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It can be seen from the above Table 1 that Examples 1, 6 and 7 gave the lowest percentage of TPE even though Examples 1-3 used the same catalyst and the same mole ratio of reactants. The conventional catalysts such as HCl (EX4), sulfonic acid (EX5A and 9 give very high levels of TPE and even oxalic acid when not used with incremental additions of glyoxal and removal of distillates also gave a high value of TPE (EX3). The post heating at 190° C in Examples 10.17H and 10.22H show no significant effect on molecular weight or free TPE but decreased in free phenol content and increased in viscosity.

TABLE 2

FLUORESCENCE DATA OBTAINED OF 0.05% SOLUTION OF THE POLYPHENOL OR EPOXIDIZED POLYPHENOL IN TETRAHYDROFURAN (THF) AT ACQUISITION TIME OF ONE SECOND AND AT AN EXCITATION WAVELENGTH OF 442 NM

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Example or Product	Maximum Intensity Counts	Wavelength Maximum, nm
1	11232	526
5A	6516	532
5 6	11502	538
7	10535	532
EPON 1031*	6403	528

*EPON 1031 (CAS: 7328-97-4) is a polyphenol containing tetraglycidyl ether of tetrakis (hydroxyphenyl)ethane and is sold by Shell Oil Co. of Emeryville, CA.

It can be seen from Table 2 above that Examples 1, 6 and 7 which are phenol-glyoxal condensation products of this invention had a fluorescence which was about 70% higher than Example 5A which was prepared with sulfonic acid catalyst. Similar results are shown in Tables 3 and 4 which follow.

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TABLE 3

FLUORESCENCE OF 0.05% SOLUTION OF EPOXIDIZED POLYPHENOL IN THF AT EXCITATION WAVELENGTH OF 442 NM AND ACQUISITION TIME OF 1.0 SECOND

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Material	Maximum Intensity Counts	Wavelength Maximum nm
EPON 1031	9640	527
EX 8	14,600	535

It can be seen from the above Table 3 that the product of Example 8, namely the epoxidized product of Example 6, shows about 50% more fluorescence than the commercial

product EPON 1031.

TABLE 4

FLUORESCENCE DATA OBTAINED OF 0.05% SOLUTION OF THE
5 POLYPHENOL IN TETRAHYDROFURAN (THF) AT ACQUISITION TIME
OF ONE SECOND AND AT AN EXCITATION WAVELENGTH OF 442 NM
WITH THE DATA OF THIS TABLE 4 BEING OBTAINED ON A
DIFFERENT DATE FROM THAT OF TABLES 2 AND 3.

	Example	Concentration wt.% Of The Polyphenol	Maximum Intensity, Counts	Wavelength Maximum nm
10	1	0.0500	16640	530
	1	0.0500	16300	531
	2	0.0503	13550	530
	2	0.0503	13510	529
	3	0.0500	12860	536
15	3	0.0500	12640	532
	4	0.0500	13960	523
	4	0.0490	13850	525
	5A	0.050	9920	535
	5A	0.050	9620	530
20	2*	0.0498	6940	540
	3*	0.0501	5130	530
	3*	0.0501	5280	527
	5A*	0.0503	5010	530

25 * The values for these are of the reaction mixture before
removal of catalyst.

It can be seen from Table 4 above, that
Example 1 has a fluorescence which is substantially higher

than the other examples, including Examples 2 and 3 which used the same catalyst in the same mole ratio of reactants.

Table 5

ULTRA VIOLET (UV) ABSORBANCE DATA IN

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DILUTE TETRAHYDROFURAN (10 MG/100 ML)

	Material	At 350 nm	At 365 nm
	Example 1	0.544	0.300
	Example 2	0.470	0.258
	Example 3	0.500	0.270
10	Example 5A	0.367	0.220
	EP* of Example 5A	0.290	0.168
	Example 6	0.515	0.288
	Example 8	0.400	0.223
	Example 9	0.266	0.134
15	EX10.17	0.385	0.216
	EX10.17H	0.416	0.224
	EX10.22	0.418	0.239
	EX10.22H	0.470	0.258
	EX11	0.728, 0.739	0.395, 0.404
20	EX12	0.465	0.317
	Epon 1031	0.273	0.161
	Pure TPE	0.000	0.000

* Epoxide

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It can be seen from the above Table 5 that Example 1 and Example 11 afford the highest absorbance at both 350 and 365 nm. All of the oxalic acid catalyzed products gave higher absorbance as compared to the sulfonic acid

catalyzed products of Examples 5A and 9. All other things being equal, the greater concentrations of TPE provide lower optical properties. Also, it should be noted that TPE shows no absorbance under the test conditions. It can also be seen that the phenol-glyoxal condensation products of Example 10 and Example 11 which were heated at 190° C for one hour, namely EX10.17H, EX10.22H and EX11 had better optical properties as compared to the product before such heating, namely EX10.17 and EX10.22. Additionally, it can be seen that the epoxidized product of Example 6, namely Example 8, gave significantly higher absorbance than the commercial product EPON 1031. Although the product of Example 12 showed high absorbance values, its viscosity was unduly high, namely, over 9000 cps at 175° C as shown in Table 1 above, and thus unacceptable.

TABLE 6
VISCOSITIES AND WEIGHT PER EPOXY EQUIVALENTS (WPE)

Material	Mw/Mn	Viscosity, cps	WPE
EPON 1031	895/395	14880 (100° C) 997 (125° C) 172 (150° C)	216
EPOXIDE of Example 6	576/348	12210 (100° C) 1580 (125° C) 440 (150° C)	214
Epoxide of Example 5A	767/374	11580 (100° C) 821 (125° C) 142 (150° C)	233

TABLE 7

FLUORESCENCE OBTAINED OF PRODUCTS IN 0.05% SOLUTION IN THF AT EXCITATION WAVELENGTHS OF 442 NM BUT AT ACQUISITION TIME OF ONE-HALF OF A SECOND.

<u>Product of</u>	<u>Counts at Maximum Intensity</u>	<u>Wavelength Maximum nm</u>
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		39	
	EX6	19,960.	531
	EX11	17,390	532
	EX10.22	19,040	530
	EX10.22H	19,940	530
5	EX10.17H	20,120	530

TABLE 8

SOLUBILITY OF CONDENSATION PRODUCTS

Solubility at 50% acetone was attempted with the various phenol-glyoxal condensates. A large vial 7/8 inches in internal diameter was charged with 10 g each of acetone and solid, warmed with vigorous agitation and then allowed to settle for 10 days at room temperature. The total height of the mixes was 1.75 inches. The clear supernatant layer was measured and is reported below in millimeters (mm). Lower values are indicative of lower solubility.

<u>Material</u>	<u>Clear Liquor, mm</u>
EX1	32
EX2	30EX48
20 EX5A	23
EX10.17	17
EX10.22	22
EX6	41
EX9	7
25 EX11	24

Several materials were checked for 50% solubility in methyl ethyl ketone. The product of Examples 1-3 and 11 remained completely soluble at room temperature after standing 10 days. Product from Example 5A deposited some product after standing 3 days.

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TABLE 9

METAL ION CONTENTS OF POLYPHENOLS & EPON 1031

Metal		EPON				
<u>Ion</u>	<u>EX1</u>	<u>EX6</u>	<u>EX7</u>	<u>EX5A</u>	<u>1031</u>	
5 Na	0.003	0.001	0.002	0.017	0.028	Ca
0.002	0.001	0.001	<0.001		0.001	
Fe	<0.001	<0.001	0.001	<0.001	<0.001	
K	0.008	<0.001	<0.001	<0.001	0.001	

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What is claimed is:

1. A method for preparing a phenol-glyoxal condensation product from a monohydric phenol and glyoxal which
5 comprises:
 - (a) charging phenol to a reaction vessel and incrementally charging a total of about 0.15 to 0.22 moles of glyoxal for each mole of the phenol charged to the reaction vessel to form a reaction mixture at a temperature of about 80° C to 100° C
10 in the presence of about 1% to 6%, based on the weight of phenol charged, of an acid catalyst which can be removed from the reaction mixture by heating and distilling the reaction mixture at a temperature below about 170° C, said catalyst selected from the group consisting of oxalic acid,
15 trichloroacetic acid and trifluoroacetic acid;
 - (b) incrementally removing water from the reaction mixture;
 - (c) maintaining the aldehyde units in the reaction mixture at less than about 70% of the aldehyde units in the total quantity of glyoxal to be charged for making the condensation
20 product;
 - (d) distilling the reaction mixture at a temperature of less than about 170° C to remove the acid catalyst when at least 85% of the aldehyde units in the total quantity of glyoxal to be charged for making the condensation product have reacted,
25 provided that prior to such distillation, a basic material is added to the reaction mixture in an amount sufficient to neutralize hydrochloric acid when the catalyst is trichloroacetic acid;
 - (e) heating the reaction mixture at a temperature of about
30 175° C to 200° C for about 0.25 hours to 3 hours after step (d) above; and
 - (f) removing unreacted phenol from the reaction mixture to obtain a phenol-glyoxal condensation product containing less than about 5% by weight of phenol.

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2. The method of claim 1 wherein the aldehyde units are measured as aldehyde equivalents.

3. The method of claim 2 wherein the incremental additions of the glyoxal are continuous additions.
4. The method of claim 2 wherein the acid catalyst is
5 selected from the group consisting of trifluoroacetic acid and oxalic acid and the reaction mixture is heated at a temperature of about 180° to 195° C for about 0.5 to 2 hours after removal of the catalyst.
- 10 5. The method of claim 2 wherein:
 (a) the phenol is a mononuclear monohydroxy phenol having from 6 to 12 carbon atoms;
 (b) the catalyst is oxalic acid in a quantity of about 3% to 5%;
15 (c) the total number of incremental glyoxal additions is from about 2 to 4;
 (d) water is distilled from the reaction mixture following reaction after each addition of glyoxal; and
 (e) the aldehyde equivalents are maintained at less
20 than about 60% of the aldehyde equivalents in the total quantity of glyoxal to be charged for making the condensation product.
6. The method of claim 2 wherein the reaction mixture is
25 distilled to remove the acid catalyst when at least about 90% of the aldehyde equivalents of the total quantity of glyoxal to be charged to the reaction mixture for making the condensation product have reacted.
- 30 7. The method of claim 2 wherein the phenol is phenol itself and the phenol-glyoxal condensation product contains from about 1% to about 6% of tetrakis(4-hydroxyphenyl) ethane.
- 35 8. The method of claim 2 wherein the phenol-glyoxal condensation product contains less than about 1.5% of unreacted phenol.

9. The method of claim 2 wherein the phenol-glyoxal condensation product has an ultraviolet absorbance of at least 0.260 at 365 nm and/or 0.400 at 350 nm.

5 10. The method of claim 2 wherein the catalyst is oxalic acid in a quantity of about 3% to 5%; the phenol is phenol itself; the aldehyde equivalents in the reaction mixture are maintained at less than about 60% of the aldehyde equivalents in the total quantity of glyoxal to be charged
10 to the reaction mixture for making the condensation product; two to four additions of glyoxal are made to the reaction mixture; a distillation of water is conducted after each addition of glyoxal and reaction of glyoxal with phenol prior to increasing the temperature above about 130°
15 C to remove the catalyst; the amount of unreacted phenol in the phenol-glyoxal condensation product is less than about 4%; and the ultraviolet absorbance of the product is at least 0.275 at 365 nm and/or 0.450 at 350 nm.

20 11. The phenol-glyoxal condensation product produced by the method of claim 2.

12. The phenol-glyoxal condensation product produced by the method of claim 10.

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13. A method for preparing a phenol-glyoxal condensation product from a monohydric phenol and glyoxal which comprises:

(a) charging phenol to a reaction vessel and incrementally
30 charging a total of about 0.15 to 0.22 moles of glyoxal for each mole of the phenol charged to the reaction vessel to form a reaction mixture at a temperature of about 80° C to 100° C in the presence of about 1% to 4%, based on the weight of phenol charged, of trichloroacetic acid as a
35 catalyst;

(b) incrementally removing water from the reaction mixture;

- (c) maintaining the aldehyde equivalents in the reaction mixture at less than about 70% of the aldehyde equivalents in the total quantity of glyoxal to be charged for making the condensation product;
- 5 (d) adding a basic material to the reaction mixture in an amount sufficient to neutralize any hydrochloric acid formed when at least 85% of the aldehyde equivalents in the total quantity of glyoxal to be charged for making the condensation product have reacted;
- 10 (e) distilling the reaction mixture at a temperature of less than about 170° C to remove the acid catalyst;
- (f) heating the reaction mixture at a temperature of about 175° C to 200° C for about 0.25 hours to 3 hours after removal of the catalyst; and
- 15 (g) removing unreacted phenol from the reaction mixture to obtain a phenol-glyoxal condensation product containing less than about 5% by weight of phenol.

14. A method for preparing a phenol-glyoxal condensation
20 product which comprises:
- (a) charging, to a reaction vessel, a monohydric, mononuclear phenol having up to 12 carbon atoms and from about 0.06 to 0.11 moles of a 40% solution of glyoxal in water, the quantity of glyoxal based on the moles of phenol
25 charged, to form a reaction mixture and wherein the reaction mixture is at a temperature of about 80° C to 100° C in the presence of about 3 to 5% of oxalic acid;
- (b) conducting a first distillation of the reaction mixture at said reaction temperature after about 1 to 5
30 hours from initial reaction of the phenol with the glyoxal in the reaction mixture and removing about 8% to 12% by weight of distillate, based on the quantity of phenol charged, from the reaction mixture;
- (c) charging to the reaction mixture another 0.06 to 0.11
35 moles of the glyoxal based on the moles of phenol charged wherein the total quantity of glyoxal charged to the reaction mixture is from about 0.15 to 0.22 moles of

- glyoxal for each mole of the phenol charged and continuing the reaction at the said reaction temperature for about another 1.5 to 6 hours after the commencement of the first distillation and then conducting a second distillation of the reaction mixture at the said reaction temperature to remove from about another 4% to 12% by weight of distillate based on the quantity of phenol charged;
- (d) continuing the reaction after the second distillation at the reaction temperature until at least 85% of the aldehyde equivalents of the total quantity of glyoxal to be charged for making the condensation product have reacted;
- (e) raising the temperature above about 130° C to about 170° C and distilling the reaction mixture to eliminate the catalyst;
- (f) heating the reaction mixture at a temperature of about 175° C to 200° C for about 0.25 hours to 3 hours after removal of the catalyst; and
- (g) removing unreacted phenol to recover a phenol-glyoxal condensation product containing not more than about 5% of unreacted phenol.
15. The method of claim 14 wherein the reaction mixture is heated at a temperature of about 190° C to 200° C for about 0.5 to about 3 hours after removal of the catalyst.
16. The method of claim 14 wherein the phenol-glyoxal condensation product has an ultraviolet absorbance of at least 0.260 at 365 nm and/or 0.400 at 350 nm.
17. The method of claim 14 wherein the catalyst is oxalic acid dihydrate; the first distillation of the reaction mixture is after about 1.5 to 3 hours from initial reaction of the phenol with the glyoxal; the second distillation is about 1.5 to 5 hours from the time the first distillation is started; and the reaction is continued for another 0.5 to 6 hours after commencement of the second distillation until at least 85% of the aldehyde equivalents of the

total quantity of glyoxal to be charged for making the condensation product have reacted.

18. The method of claim 14 wherein the reaction
5 temperature is from about 85° C to about 95° C.

19. The method of claim 14 wherein the phenol is phenol
itself and the phenol-glyoxal condensation product contains
from about 1% to about 6% of tetrakis(4-hydroxyphenyl)
10 ethane.

20. The phenol-glyoxal condensation product produced by
the method of claim 14.

15 21. A phenol-glyoxal condensation product having an
ultraviolet absorbance of at least 0.260 at 365 nm and/or
0.400 at 350 nm.

22. The phenol-glyoxal condensation product of claim 21
containing from about 0% to about 6% of TPE.

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23. The phenol-glyoxal condensation product of claim 21
wherein
the phenol is phenol itself.

25 24. The product of claim 21 containing a concentration of
less than: about 0.005% of sodium; about 0.003% of calcium;
about 0.003% of iron; and about 0.002% of potassium.

25. An epoxy resin selected from the group consisting of a
30 glycidylated phenol-glyoxal condensation product of claim
21, a reaction product of about 4 to 8 parts of a glycidyl
epoxy resin to each part of a diglycidylated epoxy resin of
claim 21, and mixtures thereof.

35 26. The epoxy resin of claim 25 having an epoxy equivalent
weight of at least 140.

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AMENDED CLAIMS

[received by the International Bureau on 09 June 1999 (09.06.99);
new claims 32-34 added; remaining claims unchanged (2 pages)]

27. A composition comprising a flame retardant epoxy resin and based on each 100 parts of said flame retardant epoxy resin:

(a) about 18 to 25 parts of a phenol-formaldehyde novolac resin; and

(b) about 3 to 10 parts of a member selected from the group consisting of an epoxy resin of claim 25, a phenol glyoxal condensation product of claim 21, and mixtures thereof.

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28. The composition of claim 27 wherein the flame retardant epoxy resin is a halogenated epoxy resin.

29. A composition comprising about 50 to 90 parts by weight of a phenolic novolac having an ultraviolet absorbance of less than about 0.260 at 365 nm and/or 0.400 at 350 nm. and 10 to 50 parts of phenol-glyoxal condensation product having an ultraviolet absorbance of at least 0.260 at 365 nm and/or 0.400 at 350 nm.

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30. The glycidylated phenol-glyoxal condensation product of claim 21.

31. The glycidylated product of claim 30 having an ultraviolet absorbance of at least about 0.200 at 365 nm and/or 0.300 at 350 nm.

32. A laminate having improved fluorescence, said laminate prepared from a composition comprising an epoxy resin and for each 100 parts of said epoxy resin:

(a) about 18 to 25 parts of a phenol-formaldehyde novolac resin; and

(b) about 3 to 10 parts of a member selected from the group consisting of,

(i) a phenol-glyoxal condensation product of claim 21,
(ii) a glycidylated phenol-glyoxal condensation product of claim 21,

(iii) a reaction product of an epoxy resin and the phenol-glyoxal condensation product of claim 21, and
(iv) mixtures thereof.

5 33. A laminate of claim 32 wherein the epoxy resin is a flame retardant epoxy resin.

34. A laminate of claim 33 wherein the flame retardant resin is a halogenated epoxy resin.

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