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(57) Abstract

Novel nitrogen–containing epoxy resin compositions suitable for photoimageable coating applications such as solder mask coating formulations are prepared by advancing an epoxy resin such as epoxy novolac resins with a nitrogen–containing compound such as diphenylmethane diisocyanate; then acrylating the advanced epoxy resin with an acrylation material such as acrylic acid, and then esterifying the advanced acrylated epoxy resin such as a novolac acrylate with an anhydride such as methylhexahydrophthalic anhydride.

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NITROGEN-CONTAINING EPOXY RESINS FOR PHOTOCURABLE COATING APPLICATIONS

The present invention relates to novel nitrogen-containing epoxy resin compositions suitable for use in photocurable compositions, including photoresist materials such as solder mask coating formulations.

Canadian Patent Application Publication No. 2,127,203 discloses epoxy acrylates and carboxyl group-containing epoxy acrylates of higher molecular weight for use in photoresist formulations.

Canadian Patent Application Publication No. 2,127,238 discloses photopolymerizable compositions for use as photoresists, such as for coating printed circuit boards and for making solder masks.

It is desired to provide (1) novel intermediate compositions useful for making novel photopolymerizable compositions and (2) novel photopolymerizable compositions including, for example, a modified epoxy novolac resin formulation that has improved adhesion on substrates and higher photospeed when the modified epoxy novolac resin contains a nitrogen element.

One embodiment of the present invention is directed to an acrylated epoxy resin composition useful as an intermediate for a photocurable resin composition, said acrylated epoxy resin prepared by reacting:

(a) an epoxy adduct made by reacting

(i) an epoxy resin having two or more epoxides, and

(ii) a nitrogen-containing monomer compound; and

(b) an unsaturated carboxylic acid.

Another embodiment of the present invention is directed to a half-ester resin composition useful for a photocurable resin composition, said half-ester prepared by reacting:

(a)the acrylated epoxy resin described above; and

(b) an anhydride compound.

Still another embodiment of the present invention is directed to a photocurable composition prepared by mixing:

(a) the half-ester resin described above;

(b) a photoinitiator;

(c) a sensitizor;

(d) a hardener catalyst;

(e) a solid epoxy novolac resin; and

(f) a reactive diluent.

Another aspect of the present invention is directed to a process for making an acrylated epoxy resin composition comprising reacting:

(a) an epoxy adduct made by reacting

(i) an epoxy resin having two or more epoxides, and

(ii) a nitrogen-containing monomer compound; and

(b) an unsaturated carboxylic acid.

Another aspect of the present invention is directed to a process for making a half-ester resin composition useful for a photocurable resin composition comprising reacting:

(a) the acrylated epoxy resin described above; and

(b) an anhydride compound.

Still another aspect of the present invention is directed to a process for making a photocurable composition comprising mixing:

(a)the half-ester resin described above;

(b) a photoinitiator;

(c) a sensitizor;

(d) a hardener catalyst;

(e) a solid epoxy novolac resin; and

(f) a reactive diluent.

Yet another aspect of the present invention is directed to a cured product such as a cured coating on a substrate including: (a) the photocurable composition described above and (b) a curing source such as a radiation energy source, for example, electron beam, ultra violet (UV) light, microwave, infrared light or heat.

The compositions of the present invention are directed to photoresist materials such as solder mask coating formulations based on nitrogen element-containing epoxy resins obtained, for example, from the advanced products of (a) epoxy novolacs such as D.E.N.™ 438 (Trademark of The Dow Chemical Company) and (b) nitrogen-containing compounds such as methylene diphenyl diisocyanate, toluene diisocyanate (TDI), sulfanilamide and 2,6-dimethylcyclohexylamine.

One of the key features required of a photoimageable epoxy polymer resin for solder mask applications is that the base epoxy polymer have a softening point of greater than or equal to 50°C. The advanced epoxy product of the present invention, that is, a nitrogen element modified-epoxy resin of the present invention, has a higher softening point and a higher molecular weight than an unmodified-epoxy resin. For example, the difference in softening point of a nitrogen element modified epoxy resin of the present invention from the softening point of an unmodified epoxy resin can be from 10°C to 60°C higher and preferably from 20°C to 50°C higher. The difference (Δ) in molecular weight as measured by epoxy equivalent weight (EEW) of a nitrogen element modified epoxy resin of the present invention from the molecular weight of an unmodified epoxy resin can be from 15 EEW to 250 EEW Δ molecular weight higher, preferably from 20 EEW to 160 EEW higher, more preferably from 25 EEW to 120 EEW higher and even more preferably from 30 EEW to 80 EEW higher.

In addition, modified epoxy-functional resins, for example, polyisocyanate-modified epoxy resins, have been shown to exhibit improved adhesion to a coated substrate and higher photospeed than unmodified-epoxy resins (for example, cresol novolacs or phenol novolac epoxy resins). For example, the difference in adhesion of a nitrogen element modified-epoxy resin of the present invention from the adhesion of an unmodified-epoxy resin can be from 5 percent to 50 percent higher and preferably from 10 percent to 30 percent higher. The difference in photospeed of a nitrogen element modified-epoxy resin of the present invention from the photospeed of an unmodified-epoxy resin can be from 10 percent to 100 percent higher and preferably from 20 percent to 50 percent higher. The epoxy resin compositions of the present invention advantageously provide improved adhesion on a substrate and higher photospeed when the epoxy resin composition is modified to contain a nitrogen element.

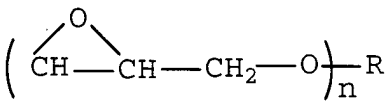
In accordance with the present invention, it has been found that certain reaction products of an adduct of polyepoxide resin compounds and nitrogen-containing advancement monomer compounds unexpectedly provide useful properties when such

compositions of the present invention are used as compositions in preparing photoresist resin compositions.

The starting materials of the present invention include (a) a polyepoxide resin and (b) a nitrogen-containing advancement monomer compound which are reacted together to form a nitrogen-containing modified advanced polyepoxide resin. The advanced polyepoxide advantageously has an increased softening point, for example, greater than or equal to 50°C. After the advanced polyepoxide is formed, the advanced polyepoxide is acrylated and then anhydride modified to produce a free-radical photocurable resin which can be lithographically developed with aqueous solutions. Such photocurable resin products are useful in the electronic coatings industry; particularly for the formulation of solder masks.

The polyepoxide compound useful in the practice of the present invention is suitably a compound which possesses more than one 1,2-epoxy group. In general, the polyepoxide compound is a saturated or unsaturated aliphatic, cycloaliphatic, aromatic or heterocyclic compound which possesses more than one 1,2-epoxy group. The polyepoxide compound can be substituted with one or more substituents which are non-reactive with the nitrogen-containing groups of the advancement polymer such as lower alkyls and halogens. Such polyepoxide compounds are well known in the art. Illustrative polyepoxide compounds useful in the practice of the present invention are described in the Handbook of Epoxy Resins, by H. E. Lee and K. Neville, published in 1967 by McGraw-Hill, New York and U.S. Patent No. 4,066,628.

Particularly useful polyepoxide compounds which can be used in the practice of the present invention are polyexpoxides having the following general formula:

Formula I: 

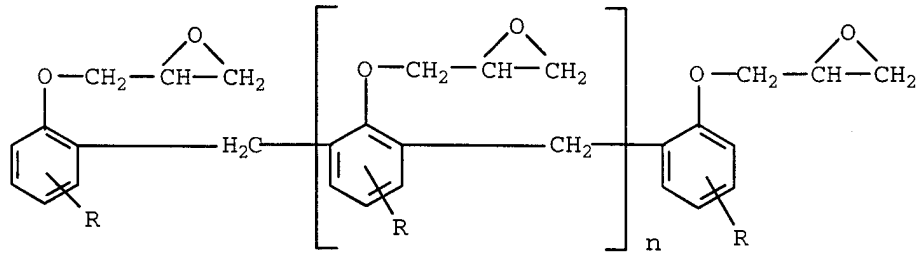
wherein "R" is a substituted or unsubstituted aromatic, aliphatic, cycloaliphatic or heterocyclic polyvalent group and "n" has an average value of from greater than 1 to less than 10. Preferably, epoxy novolac resins and diepoxide resins are used in the present invention.

The diepoxides which may be used in the present invention include, for example, diglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane (generally referred to as bisphenol A) and diglycidyl ether of 2,2,-bis(3,5-dibromo-4-hydroxyphenyl)propane (generally referred to as tetrabromobisphenol A). Diepoxides also useful in the present invention include, for

example, diglycidyl ether of 4,4'-dihydroxy-alpha-methylstilbene (DHAMS) and diglycidyl ether of 9,9-bis(4-hydroxyphenyl)fluorene (BHPF). Mixtures of any two or more polyepoxides can also be used in the practice of the present invention.

The more preferred polyepoxides used in the practice of the present invention are the epoxy novolac resins. Epoxy novolac resins (sometimes referred to as epoxidized novolac resins, a term which is intended to embrace both epoxy phenol novolac resins and epoxy cresol novolac resins) are polyepoxy compounds having the following general formula:

Formula II:



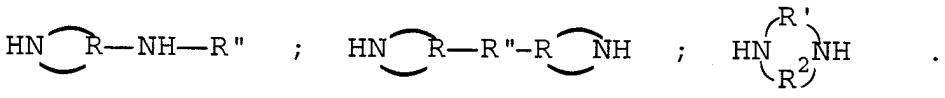
wherein "R" is a hydrogen atom or a lower alkyl, for example, methyl groups; and "n" is 0 or an integer from 1 to 6.

Epoxy novolac resins (including epoxy cresol novolac resins) are readily commercially available, for example, under the trademark D.E.N.™, QUATREX™, Grilonit™ (ESN) and Araldite™ (ECN). The materials of commerce generally comprise mixtures of various species of the above formula and a convenient way of characterizing such mixtures is by reference to the average, n', of the values of n for the various species. Preferred epoxy novolac resins for use in accordance with the present invention are those in which n' has a value of from 2.05 to 10, more preferably from 3 to 5.

The nitrogen-containing advancement monomers useful in the practice of the present invention are selected from isocyanates, amines and amides.

The nitrogen-containing advancement monomers useful in the practice of the present invention include, for example, polyisocyanate compounds which form epoxy-terminated polyoxazolidones as described in U.S. Patent No. 5,112,932. Preferably, the polyisocyanate compound used in the present invention is 4,4'-methylene bis(phenylisocyanate) (MDI) and isomers thereof and functional homologs of MDI (commonly designated as "polymeric MDI"). Isocyanate compounds also useful in the present invention include, for example, toluene diisocyanate (TDI) and isomers thereof.

The nitrogen-containing advancement monomers useful in the practice of the present invention also include, for example, amine- or amino amide-containing compounds which form epoxy-terminated amine compounds having two N-H bonds capable of reacting with an epoxy group. Amine-containing compounds useful in the present invention include, for example, mono-primary amines of the general formula R-NH_2 wherein R is alkyl, cycloalkyl or aryl moieties; di-secondary amines of the general formula R-NH-R'-NH-R" wherein R, R' and R" are alkyl, cycloalkyl or aryl moieties; and heterocyclic di-secondary amines wherein one or both of the N atom is part of a nitrogen-containing heterocyclic compound such as:



For reactivity reasons, and in order to better control the epoxy advancement reaction with the di-functional amines, di-secondary amines or primary amines having sterically hindered amine groups are preferred as for example, 2,6-dimethylcyclohexylamine or 2,6-xylidene (1-amino-2,6-dimethylbenzene).

Amino amide-containing compounds useful as advancement monomers in the present invention include for example, derivatives of carboxylic acids and amides as well as derivatives of sulfonic acid amides having additionally one primary or two secondary amino groups. Preferred examples of such compounds are amino-aryl carboxylic acid amides and amino-arylsulfonamides. A preferred compound of this group is, for example, sulfanilamide (4-amino benzylsulfonic acid amide).

After the advanced polyepoxide resin is obtained by reacting a polyepoxide with a nitrogen-containing advancement monomer as described above, the advanced polyepoxide is acrylated to form an epoxy acrylate. The acrylation of the advanced epoxy resins is preferably carried out with an unsaturated carboxylic acid, for example, acrylic or methacrylic acid. More preferably, an acrylic acid is used in the present invention. Other acrylation materials include, for example, trans-3-phenyl acrylic acid.

After the epoxy acrylate resin is obtained by reacting the advanced polyepoxide with an acrylation material as described above, the epoxy acrylate resin is esterified with an unsaturated or saturated anhydride to form a half-ester. The anhydride materials useful in the practice of the present invention include, for example, the saturated carboxylic acid anhydrides described in the Handbook of Epoxy Resins, by Lee and Neville in Page 12-6 including, for example, succinic anhydride, alkenyl anhydride,

dodecenylsuccinic anhdyride, hexahydrophthalic anhydride, phthalic anhydride, and methylhexahydrophthalic acid anhydride (MHHPA). The anhydride esterification reaction to the half-ester of the epoxy acrylate resin is preferably carried out with MHHPA.

The anhydride modified advanced epoxy resin acrylate described above is the product which can be used as a photoresist material. Photoresist materials include for example, photoimageable resins for solder mask applications and etch resist applications. Other photoresist materials include, for example, plating resists.

The process of preparing the photocurable compositions of the present invention comprises the steps of (1) reacting a polyepoxide resin and a nitrogen-containing advancement monomer compound together to form a nitrogen-containing modified advanced polyepoxide resin; (2) reacting the advanced polyepoxide of Step (1) above with an acrylation material to form an epoxy acrylate; and (3) reacting the epoxy acrylate resin of Step (2) above with an unsaturated or saturated anhydride to form a half-ester.

In one embodiment of the present invention, a nitrogen-containing epoxy resin useful for photoimageable coating applications includes (1) advancing a low molecular weight epoxy novolac resin with a nitrogen-containing compound such as diphenylmethane diisocyanate, (2) fully acrylating the advanced epoxy novolac resin with acrylic acid, and (3) esterifying the acrylated resin to the half-ester with methylhexahydrophthalic anhydride.

The process steps of the present invention are generally carried out under reaction conditions, that is, temperatures and pressures that allow the reaction to proceed. Optionally, ingredients that do not adversely effect the reaction may be used; for example, a catalyst may be used in each of the reaction steps of the present process.

As an illustration of the present invention, the advancement reaction such as the reaction of an epoxy novolac resin(s) with an amine-containing compound(s) is carried out by reacting the epoxy novolac resin with the amine-containing compound, generally at temperatures of from 60°C to 200°C, preferably from 100°C to 150°C and optionally, the reaction is carried out in the presence of a catalyst.

In another embodiment of the present invention, the advancement reaction such as reaction of an epoxy novolac resin(s) with an isocyanate compound(s) is carried out by reacting the epoxy novolac resin with the isocyanate compound, generally at temperatures of from 120°C to 200°C, preferably from 150°C to 180°C, in the presence of a catalyst. The catalysts useful in the advancement reaction step include for example, tertiary amines, phosphines, imidazoles, and ammonium and phosphonium salts. Examples of the

catalysts useful in this reaction step include quaternary ammonium and phosphonium salts such as tetraphenylphosphonium chloride; tertiary amines; nitrogen-containing heterocycles such as: substituted imidazoles including 1-methylimidazole, 2-methylimidazole, 1-phenylimidazole, 2-phenylimidazole, benzimidazole, 2-ethyl-4-methylimidazole, 1-benzyl, 2-phenylimidazole, 1-cyanoethyl-2-phenylimidazole; 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,8-diazabicyclo[5.4.0]undecene-7 (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN); substituted phosphines such as triphenylphosphine and mixtures thereof. The preferred catalysts useful in this step are the substituted imidazoles, most preferably 1-phenylimidazole, 2-phenylimidazole, and DBU or DBN. Above 200°C, the advancement reaction is not economically effective and below 60°C, the advancement reaction is too slow to be effective.

In the acrylation step of the process of the present invention, the reaction temperature is generally from 80°C to 150°C, preferably 100°C to 130°C. The acrylation reaction step requires a catalyst, for example, when reacting an advanced epoxy with acrylic acid. The catalyst useful in this step can be for example, tertiary amines such as triethylamine, tributylamine, triphenylamine, benzyldimethylamine, tris(dimethylaminomethyl)phenol; phosphines such as triphenylphosphine; imidazoles such as 1-methylimidazole, 2-methylimidazole, 1-phenylimidazole, 2-phenylimidazole, benzimidazole, 2-ethyl-4-methylimidazole, 1-benzyl, 2-phenylimidazole; heterocyclic amino compounds such as: benzotriazole, pyridine, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 2,3-dimethylpyridine, 2,4- or 2,5 or 2,6-dimethylpyridine, 2,4,6-trimethylpyridine, quinoline, N,N-dimethyl-4-amino-pyridine; quaternary ammonium and phosphonium salts such as tetramethylammonium bromide, tetrabutylammonium chloride, tetraethylammonium iodide, dimethylbenzylammonium chloride, tetraphenylphosphonium chloride, ethyltriphenylphosphonium acetate; organic or inorganic metal salts such as chromium chloride, chromium acetate and mixtures thereof.

The acrylation reaction also requires an inhibitor to stop the double bond compounds such as acrylic acid from reacting or polymerizing with itself, that is, the inhibitor is used to prevent radical polymerization. Examples of inhibitors useful in the acrylation step include, for example, hydroquinone and those described in U.S. Patent No. 4,413,105. A solvent is optionally used in the acrylation reaction step to control the reaction mixture viscosity and better control the reaction. For example when a high molecular weight material is used, a solvent can be optionally used. Examples of solvents useful in this step include,

for example, those solvents having a boiling point higher than 110°C and do not react with any of the components of the present composition such as Dowanol™ PMA or xylene or toluene. The acrylation reaction step also requires the use of an oxygen-containing stream such as air to help activate the inhibitor.

The acrylation step of the process of the present invention, is carried out such that all or 100 percent of the epoxy groups on the advanced polyepoxide are reacted with acrylic acid groups, preferably from 75 percent to 100 percent, more preferably from 85 percent to 99 percent, and most preferably from 90 percent to 97 percent of the epoxy groups are reacted. The acrylation reaction step is carried out to provide a residual acid percentage of the resin of generally less than about 1 percent, preferably less than about 0.5 percent, more preferably less than about 0.2 percent and most preferably less than about 0.1 percent.

The esterification of the advanced acrylated epoxy resin is generally carried out at temperatures of from 80°C to 130°C, preferably from 110°C to 130°C. Optionally, this esterification step is carried out in the presence of a catalyst such as those used in the acrylation step above including for example, a tertiary amine, phosphine, ammonium or phosphonium salt or a metal salt of an organic or inorganic acid. Also, a solvent may be optionally used in this esterification step. Preferably, the solvent used is not a hydroxy-containing solvent because the hydroxy-containing solvent can react with the anhydride groups. During the esterification reaction step the resin contains an acid value generally in the range of from 20 to 200, preferably from 50 to 150, more preferably from 80 to 120 and most preferably from 90 to 105 acid value.

The present invention is also directed to a process for making a photocurable composition comprising mixing or blending together:

(a) the half-ester resin described above;

(b) a photoinitiator;

(c) a sensitizor;

(d) a hardener catalyst;

(e) a solid epoxy novolac resin; and

(f) a reactive diluent.

The photocurable materials (esters) in accordance with the present invention are readily photocurable by the action of ultra violet light in the presence of a conventional photoinitiator.

The present invention accordingly, provides a photocurable composition comprising a photocurable material as defined above together with a photoinitiator. Such compositions may also, and indeed, generally will, contain other ingredients such as, for example, diluents, colorants or fillers.

Suitable photosensitizers or photoinitiators for use in the photocurable compositions of the present invention include, for example, benzophenone, substituted benzophenones, 2-chlorothioxanthone, isopropylthioxanthene, dialkyl-p-dimethylamine benzoates (including the diethyl, amyl/isoamyl and ethyl hexyl compounds), and 2-cleavage initiators, such as those sold under the trademarks Darocur™ 1173, Irgacure™ 174, Irgacure™ 184, Irgacure™ 651, Irgacure™ 907, Irgacure™ 369, Esacure™ KIP, and Lucirin™ 7PO. Commonly, an initiator system will comprise a mixture of two or more compounds as listed above.

Examples of diluents possibly employed in the photocurable compositions of the present invention may be tris(2-hydroxyethyl)isocyanate triacrylate and trimethylol propane triacrylate.

The colorants which may be used in the photocurable composition of the present invention may be selected from phthalocyanine green and methylene blue.

Suitable fillers which can be used in the photocurable composition of the present invention may include, for example, silicas, bentonite clays, talc, alumina hydrate, barium sulfate, calcium carbonate and magnesium carbonate.

In accordance with a particularly preferred embodiment of the present invention, the photocurable composition generally comprises (I) an epoxy, (II) a diluent, (III) a photoinitiator, and (IV) a colorant. The photocurable composition suitably comprises from 10 to 95 percent by weight (weight percent), preferably from 20 to 70 weight percent of (I); from 1 to 20 weight percent, preferably from 2 to 10 weight percent of (II); from 0.001 to 10 weight percent, preferably from 0.05 to 3 weight percent of (III); and from 0.01 to 10 weight percent, preferably from 0.1 to 5 weight percent of (IV).

The compositions of the present invention are useful as photoresist materials, such as etch resist and solder mask-coating formulations. Typically, a 1-component or 2-component system can be formulated to provide the photoresist product.

Examples of a 1-component system are described in U.S. Patent No. 5,049,628; EP 418011; WO 89/07785; and EP 359216. Examples of a 2-component system are described in U.S. Patent No. 5,009,982; GB 2,273,707; EP 292219 and EP 306273.

The coating formulations are applied to substrates as is known in the art. The coating formulation (or varnish as sometimes referred) on the substrates, such as metal or circuit board epoxy resin laminates, is cured with an energy curing source, such as UV light, infrared light or heat. The cured coating on the substrate can then be tested for use as a solder mask-coating in electronic applications.

The compositions of the present invention show improvements in higher softening point and higher molecular weight than the unmodified epoxy novolac resins. For example, the polyisocyanate modified epoxy-functional resins have been shown to exhibit improved adhesion to the coated substrate and higher photospeed than the unmodified epoxy resins (cresol novolacs or phenol novolac epoxy resins).

In order to understand the present invention more fully, the following examples are given by way of illustration only and not be limited thereby. In the examples which follow all parts and percentages are by weight unless otherwise indicated.

All resin preparations in the following examples were done in the same laboratory reactor apparatus: A 1-liter flange-top glass reactor was equipped with an electrically driven mechanical stirrer, air and nitrogen inlets, a sample port, an overhead condenser, an addition funnel for liquids, an electrical heating mantel, thermocouple and temperature controller.

After production of the advanced resins, the advanced resins were analyzed for epoxy equivalent weight (EEW), melt viscosity, softening point and glass transition temperature (T_g). Melt viscosity was determined by American Standard Testing Method (ASTM) D4287. Generally, the products of the present invention contain melt viscosities of at least 50 percent higher than unmodified resins. The softening point of the resin was determined by Dow Quality Control Method Number RPM 108C; such method is described in a publication readily available from The Dow Chemical Company. The T_g of the resin was determined by using a Mettler DSC 30, an apparatus commercially from Mettler Instrument AG (Switzerland), and scanning a sample of the resin using the Mettler DSC 30 at 10°C/minute from 0 to 150°C. The T_g of the resins of the present invention are generally 5°C higher than resins which are not modified according to the present invention, preferably 10°C higher and more preferably 15°C higher than the unmodified resins. In some

instances, the T_g of the resins of the present invention can be as much as 50°C higher than the unmodified resins.

The acrylated, acid functionalized resins produced were analyzed for acid value, solution viscosity and solids content.

A summary of the resin compositions prepared in the following Examples and their properties are described in Tables I and II.

Examples 1 to 6

Step 1: The Advancement Reaction: General Production Procedure for the Polyepoxy/Polyisocyanate Copolymers

In this step, an epoxy resin, for example, a liquid epoxy novolac (LEN) resin such as D.E.N.™ 438 or D.E.N.™ 431, commercially available from The Dow Chemical Company, was advanced with an isocyanate compound, for example, methylene diphenyl diisocyanate (MDI), to produce a polyepoxy/polyisocyanate copolymer as follows: An epoxy resin was heated up to 100°C under a nitrogen purge in a 1-liter flange-top glass reactor equipped with an electrically driven mechanical stirrer, air and nitrogen inlets, sample port, condenser and thermocouple. To the epoxy was added 1500 ppm based on the total solids (epoxy plus MDI) of 1,8-diazabicyclo(5.4.0)undecene-7, a reaction catalyst such as AMICURE™ DBU-E, commercially available from Anchor; and the mixture was heated to 130°C to 140°C. MDI such as ISONATE™ M143 commercially available from The Dow Chemical Company was charged into the epoxy resin via an addition funnel in the reactor, portion by portion within a period of time ranging from 5 minutes (for example, for D.E.N. 438) to 60 minutes (for example, for D.E.N. 431) to 120 minutes (for example, for D.E.R.™ 330) depending on the amount of MDI to be added and depending on the size of the reactor used. The reaction temperature was raised up to at least 150°C (for example, for D.E.N. 438) or 165°C (for example for D.E.N. 431) or 180°C (for example for D.E.R.™ 330) by the heat of reaction. After the end of addition, the reaction mixture was kept at the above reaction temperature for at least 1 hour until the theoretical epoxy equivalent weight (EEW) of the resultant copolymer was reached. The reaction processes are taught, for example, in U.S. Patent No. 5,112,932. The resultant copolymer resin was ready for acrylation.

Step 2: The Acrylation Reaction: General Production Procedure for the Acrylation of the Advanced Resins

In this step, the advanced resins obtained in Step 1 above were acrylated with acrylic acid as follows: The resin solution obtained after advancement in Step 1 above was further diluted with an amount of DOWANOL™ PMA calculated to obtain a constant 75 percent solid solution of epoxy acrylate. During acrylation the nitrogen purge was stopped and replaced by a bubbling of air into the reaction mixture through a glass tube plunger. The air flow was started at a rate of 2 to 3 bubbles/second and 400 ppm (based on acrylated solid) hydroquinone inhibitor was added, followed by the required amount of acrylic acid (0.98 mole acid/equivalent epoxy). Then 900 ppm (based on acrylated solid) of a 33 percent water solution of $CrCl_3 \cdot 6H_2O$ esterification catalyst was added to the reactor, and the temperature was slowly increased to the reaction temperature of 120°C to 125°C, taking care to avoid overheating due to exotherm. The acrylation reaction was continued until the percent residual acid dropped below 0.5 percent based on solids. The total acrylation time needed was 3 to 4 hours. The reaction medium was then cooled to 105°C, and 250 ppm (based on solids) of 4-methoxyphenol (MEHQ) was added into the reactor. The air flow was stopped. The resultant acrylated resin solution was ready for the half-ester reaction.

Step 3: The Esterification Reaction: General Production Procedure for the Esterification of the Acrylated Advanced Resins to the Half-ester

In this step, the acrylated resins obtained in Step 2 above were esterified to the half-ester with an anhydride such as methylhexahydrophthalic anhydride (MHHPA) as follows: The resin solution obtained in Step 2 above was further diluted with DOWANOL™ PMA to adjust the final solids content to 70 percent (65 percent for the highest viscosity resins) and the temperature was maintained at 105°C. The required amount of MHHPA (calculated to yield an acid value of 90) was then dropped into the reactor via the addition funnel. Then 750 ppm (based on final solids) of 2,4,6-tris(dimethylaminomethyl)phenol, a catalyst such as ANCAMINE™ K54 commercially available from Air Products, was charged to the reactor to catalyze the anhydride-hydroxy reaction. The temperature of the reactor was increased to 115°C to 120°C and the reaction was continued for 2 to 3 hours until the acid value of the resin dropped to a range of 90 to 105. The resultant resin was then cooled to 80°C and transferred to a metal container for storage.

The resin compositions prepared in Examples 1 to 4 and analysis of the composition's properties are given in Table I. Examples 5 and 6 were carried out using only Steps 1 and 2. The same procedure for the advancement reaction (Step 1) and the acrylation reaction (Step 2) as in Examples 1 to 4 were used for Examples 5 and 6 and the results of these examples are also described in Table I.

Comparative Example A

This example was carried out using the same procedure as in Examples 1 to 4 except that D.E.N.™ 438 was used without advancing the epoxy with the addition of MDI. The results of this Comparative Example A are described in Table I.

Comparative Example B

This example was carried out using the same procedure as in Examples 1 to 4 except that a cresol epoxy novolac (CEN) with a softening point of 79°C was used without advancing the epoxy novolac with the addition of MDI. The results of this Comparative Example B are described in Table I.

Table I: _

Composition and Characterization of LEN/MDI and LER/MDI Adducts and of Derived Solder Mask Resins

Example	1	2	3	4	5	6	Comparative Example A	Comparative Example B
LEN/MDI weight ratio	92.5/7.5	91.5/8.5	85/15	81/19	79/21	78/22	100/0	100/0
Advancement Reaction								
D.E.N.™ 438	326.9	330.0					372.4	
D.E.N.™ 431			320.5					
D.E.R.™ 354				315.0				
D.E.R.™ 330				315.0	395	390		
CEN resin with a softening point of 79°C								383.9
ISONATE™ M143[1]	26.5	30.6	56.5	73.9		110		
PAPI™ 27[1]					105			
AMICURE™ DBU-E[2](ppm based on solids)	1500	1500	1500	1500				

Table I (cont'd)

Advanced Resin Analysis								
% Epoxy	19.48	19.15	15.66	13.36	12.25	11.16	23.89	21.39
EEW	220	225	275	322	351	385	180	201
Melt Viscosity (120°C, mPa•s)	3040	4760	3840	3680	-	-	150	5840
Resin T_g (°C)	25.8	27.4	29.8	27.8	43	49	7.4	37.3
Mettler Softening Point (°C)	69.1	73.4	74.3	73.6	98	100	39.2	79.0
Acrylation Reaction								
DOWANOL™ PMA[3]	117.4	158.2	158.2	158.2	257	253.5		133.3
Hydroquinone (ppm based on solids)	400	400	400	400	400	400	400	400
Acrylic Acid	115.7	114.0	97.6	85.7	99.6	91.4	149.2	137.7
$CrCl_3 \bullet 6H_2O$ (33% in water), ppm based on Vinyl Epoxy Resin (VER)	900	900	900	900	900	900	900	900
% Epoxy	0.39	0.52	0.38	0.52	0.51	0.62	0.36	0.42
% Acid	0.18	0.38	0.24	0.33	0.08	0.27	0.25	0.29
MEHQ[4], ppm base on VER	250	250	250	250	250	250	250	250

Table I (cont'd)

Half-ester Reaction								
DOWANOL™ PMA[3]	161.1	120.4	120.3	120.4			175.5	100
MHHPA[5]	180.9	175.4	175.4	175.4			178.4	178.4
ANCAMINE™ K54[6] (ppm based on solids)	750	750	750	750			750	750
DOWANOL™ PMA[3]	71.5	71.4	71.5	71.4			124.5	66.7
Final Resin Analysis								
Solids Content (%)	65	65	65	65	60	60	70	70
Solution Viscosity (cSt., Cannon Fenske at 40°C)	4565	5770	4010	3970	-	-	3130	13310
Acid Value (based on solids)	96.4	94.5	94.8	102	0.08	0.27	87	90

(1) Isonate M143 = Methylene diphenyl diisocyanate, commercially available from The Dow Chemical Company.
PAPI 27 = Methylene diphenyl diisocyanate, commercially available from The Dow Chemical Company.

(2) AMICURE DBU-E = 1,8-diazabicyclo(5.4.0)undec-7-ene,commercially available from Anchor.

(3) DOWANOL™PMA = Methoxy propyl acetate.

(4) MEHQ = Hydroquinone monomethylether.

(5) MHHPA = Methylhexahydrophthalic acid anhydride.

(6) ANCAMINE K54 = 2,4,6-Tris(dimethylaminomethyl)phenol.

Examples 7 and 8

Step 1: The Advancement Reaction: General Production Procedure for the Polyepoxide/Amine Copolymers

In this step, an epoxy resin, for example, a liquid epoxy novolac (LEN) resin such as D.E.N.™ 438 commercially available from The Dow Chemical Company, was advanced with an amine compound, for example, 2,6-dimethylcyclohexylamine (2,6-DMCH), to produce a polyepoxide/amine copolymer as follows: The reactor was purged with nitrogen to maintain an inert atmosphere. An epoxy (for example, D.E.N. ™ 438) was preheated to 80°C and then 475 g of the preheated epoxy was charged to the reactor and heated to 90°C. To the epoxy was added 25 g of 2,6-DMCH via the addition funnel of the reactor under 80 revolutions per minute (rpm) agitation. The inside temperature of the reactor was increased to 130°C, and the reaction was continued for 2.0 hours until completion as shown by the epoxy analysis. For example, the epoxy analysis for the resultant resin using a weight ratio of D.E.N.™ 438/2,6-DMCH of 95:5 was an EEW, corrected for amine, = 218.8 (theoretical EEW = 222.6). A sample of the resultant solid resin was taken for analysis before the resin was diluted to 75 percent solids with 167 g of a solvent such as DOWANOL™ PMA (Trademark of The Dow Chemical Company). After cooling the resultant resin to 105°C, the resin was ready for further acrylation.

The above procedure was carried out using a weight ratio of D.E.N. ™ 438/2,6-DMCH of 95:5 and 94:6. The EEW obtained for the advanced resin using a weight ratio of D.E.N. ™ 438/2,6-DMCH of 95:5 was 218.8 (theoretical EEW = 222.6). The EEW obtained for the advanced resin using a weight ratio of D.E.N. 438/2,6-DMCH of 94:6 was 228.2 (theoretical EEW = 233.8). The analysis of the two advanced resins prepared in Examples 7 and 8 is described in Table II.

Step 2: The Acrylation Reaction: General Production Procedure for the Acrylation of the Advanced Resins

The acrylation reaction Step 2 used in this Example was the same as in Examples 1 to 6 above. The analysis of the resin is given in Table II.

Step 3: The Esterification Reaction: General Production Procedure for the Esterification of the Acrylated Advanced Resins to the Half-ester

The esterification reaction Step 3 used in this example was the same as in Examples 1 to 6 above. The analysis of the resin is given in Table II.

Example 9

Step 1: The Advancement Reaction: General Production Procedure for the Polyepoxide/Amine Copolymers

In this step, an epoxy resin, for example, a liquid epoxy novolac (LEN) resin such as D.E.N.™ 438, commercially available from The Dow Chemical Company, was advanced with an amine compound, for example sulfanilamide, to produce a polyepoxide/amine copolymer. In this Example, D.E.N.™. 438 was advanced in molecular weight with sulfanilamide at a weight ratio of 94:6. The final theoretical EEW was calculated for complete reaction of the primary amine, as it is known that the amide group reacts with epoxy at a much slower rate and a high temperature. The LEN advancement with sulfanilamide was carried out as follows: The reactor was purged with nitrogen to maintain an inert atmosphere. An epoxy (for example, D.E.N.™ 438) was preheated to 80°C and then 501 g of the preheated D.E.N.™ 438 was charged to the reactor and heated to 105°C. Then 32 g of sulfanilamide powder was slowly introduced into the reactor under 80 rpm agitation until complete dissolution. The inside temperature of the reactor was increased to 130°C, and the reaction was continued for 3.0 hours until the reaction was complete as shown by the epoxy analysis. In this Example, the EEW of the epoxy resin obtained was an EEW, corrected for amine = 221.1 (theoretical EEW = 221). A sample of the resultant solid resin was taken for analysis before the resin was diluted to 75 percent solids with 178 g of a solvent such as DOWANOL™ PMA. After cooling the resultant resin to 105°C, the resin was ready for further acrylation. The analysis of the resin is given in Table II.

Step 2: The Acrylation Reaction: General Production Procedure for the Acrylation of the Advanced Resins

The acrylation reaction Step 2 used in this example was the same as in Examples 1 to 6 above. The analysis of the resin is given in Table II.

Step 3: The Esterification Reaction: General Production Procedure for the Esterification of the Acrylated Advanced Resins to the Half-ester

The esterification reaction Step 3 used in this example was the same as in Examples 1 to 6 above. The analysis of the resin is given in Table II.

Comparative Example C

This example was carried out using the same procedure as in Examples 7 to 8 except that an epoxy resin, D.E.N.™ 439, was used without advancing the epoxy resin

with the addition of an amine. The results of this Comparative Example C are described in Table II below.

Table II:

Composition and Characterization of LEN/Amine Adducts and of Derived Solder Mask Resins

Example	7	7	9	Comparative Example C
LEN/Amine weight ratio	95/5	94/6	94/6	100/0
Advancement Reaction				
D.E.N.™ 438	475.0	570.0	501.0	
D.E.N.™439				500.0
2,6-DMCH[1]	25.0	30.0		
Sulfanilamide			32.0	
Advanced Resin Analysis				
% Epoxy	19.65	18.84	19.45	21.72
Melt Viscosity (120°C, mPa·s)	610	980	1460	470
Resin T_g (°C)	20.5	22.4	26.6	13.9
Mettler Softening Point (°C)	56.4	61.3	64.2	49.4
Acrylation Reaction				
DOWANOL™ PMA[2]	220	Not acrylated	235	170
Hydroquinone, ppm based on VER	400	-	400	400

Table II (cont'd)

Acrylic Acid	160	-	172	178.5
$CrCl_3 \bullet 6H_2O$ (33% in water), ppm based on VER	900	-	900	900
% Epoxy	0.44	-	0.36	
% Acid	0.27	-	0.22	
MEHQ[3], ppm based on VER	250	-	250	250
Half-ester Reaction		-		
DOWANOL™ PMA[2]	167	-	178	228.0
MHHPA[4]	244	-	260	250.5
ANCAMINE™ K54[5] (ppm, based on solids)	750	-	750	750
DOWANOL™ PMA[2]		-		
Final Resin Analysis				
Solid Content (%)	70	-	70	70
Solution Viscosity (cSt., Cannon Fenske at 40°C)	6557	-		
Acid Value, based on solids	90.8	-	92.0	

(1)2,6-DMCH = 2,6-Dimethylcyclohexylamine.

(2)DOWANOL™ PMA= Methoxy propyl acetate.

(3)MEHQ = Hydroquinone monomethylether.

(4)MHHPA = Methylhexahydrophthalic acid anhydride.

(5)ANCAMINE K54 = 2,4,6-Tris(dimethylaminomethyl)phenol.

Example 10

The accelerated shelf life stability for the following two solder mask resin solutions was carried out:

(1) The resin of Example 2; and

(2) The resin of Example 7.

The method used for measuring the accelerated shelf life stability of the above resins was as follows:

A 100 mL glass bottle was filled at 95 percent of its volume with the solder mask resin solution, then closed with a screwed cover and, finally placed in a stability oven where the inside temperature was controlled at 50°C ± 1°C. The stability of these two solder mask resin solutions was followed by measuring the viscosity increase versus the initial/starting viscosity every 5 to 10 days interval using the Canon Fenske (C.F.) viscosity method (ASTM-D445): viscosity measurement recorded at 40°C in a temperature controlled water bath.

Results: C.F. Viscosity at 40°C	Resin of Example 2	Resin of Example 7
Initial/starting viscosity	5971 cSt.	6417 cSt.
After 5 days at 50°C	6127 cSt. + 2.6%	6554 cSt. + 2.1%
After 12 days at 50°C	6226 cSt. + 4.3%	6684 cSt. + 4.2%
After 20 days at 50°C	6400 cSt. + 7.2%	6782 cSt. + 5.7 %
After 33 days at 50°C	6524 cSt. + 9.3 %	6874 cSt. + 7.1 %
After 56 days at 50°C	6722 cSt. + 12.6 %	7011 cSt. + 9.3%
After 75 days at 50°C	6921 cSt. + 15.9 %	7173 cSt. + 11.8 %

The data indicates that the resins would have a shelf life of at least six months when stored at ambient conditions.

Example 11

Preparation of Solder Mask Varnish

A solder mask varnish was prepared using the following three resins:

1. Sample A: ISONATE™ M143/438, fully acrylated and MHHPA to acid value (AV) = 96.4

   70 percent solids in Dowanol™ PMA.

2. Sample B: CEN, fully acrylated and MHHPA to AV = 87

   70 percent solids in Dowanol™ PMA.

3. Sample C: LEN (D.E.N.™ 438) fully acrylated and MHHPA to AV = 86

   70 percent solids in Dowanol™ PMA.

Each of the above resins was formulated into a typical 2-component solder mask varnish made up of Part A and Part B as described in Table III. A typical procedure for making the 2-component varnish can be found in, for example, GB 2,273,707.

Table III

Part A		Part B	
Photoimageable resin (Sample A, B or C) at 70% solids	70.0	**CEN** Solid epoxy novolac melting point = 75°C	32.9
Irgacure™ 651 photoinitiator, Ciba-Geigy	7.5	**Trimethylolpropane triacrylate** reactive diluent	16.0
Xanthone™ ITX sensitizor, Lambert Ltd.	1.3	**Talc** Filler, Harwick	27.0
Modaflow™ Flow aid, Monsanto	1.6	**Dowanol™ PMA** Solvent, The Dow Chemical Company	24.0
			100.0
Talc Filler, Harwick	13.1		
2-Ethyl-4-methylimidazole hardener catalyst, BASF	0.8		
NMP n-methylpyrrol-idone) Reactive diluent, BASF	0.8		
Micronized dicyandiamide Hardener, Anchor	0.2		
Dowanol™ PMA Solvent, The Dow Chemical Company	7.1		
Silica Dispersant aid	0.4		
Pigment Chromium dioxide	5.0		
	100.0		

Two parts of Part A was mixed with 1 part of Part B (all components being dispersed using a ball mill apparatus) to form a solder mask varnish. Test coatings were made from the varnish and the performance of each of the coatings was evaluated.

The Sequence of Testing/Comparison Process of Coatings

A. Bar coat (75 micron) of varnish onto: (1) metal panel and (2) bare FR-4 board (ED130 obtained from Allied Signal Laminate Systems GmbH, Germany).

B. Pre-exposure bake: Heat each of the panels at 120°C for 5 minutes and then place each panel on a hot plate at 35°C for 10 minutes:
TEST 1: For tackiness. This test gives plastic rating. A hard rating is required so that image negatives can be placed on the surface of the panels without sticking to the coating during the exposure process.

C. Expose panels to an H-lamp at 5.8 m/s to 1, 2, 3, 4, 5, 7 and 9 passes:
TEST 2: methyl ethyl ketone (MEK)-rub resistance on corner of panel. This test gives relative photospeed rating, good MEK-rating after minimal exposure is required; indicating fast photopolymerization. Generally, the resins of the present invention provide increased speed of greater than 5 percent, and preferably from 10 percent to 50 percent greater than the unmodified resins.

D. Post-exposure bake: Heat each of the panels at 140°C for 90 minutes:
TEST 3: MEK-rubs. This test provides an indication of the extent of cure/adhesion on a panel substrate.
TEST 4: Cross-hatch resistance on coated FR-4 boards was carried out using ASTM D 3359-83 Method B. In this test a result of 00 is the best and 55 is the worst. Generally the coatings of the present invention had a cross-hatch resistance of 00 to 11.
TEST 5: Impact test on coated metal panels (1 kg used, inch ball) was carried out in accordance with ASTM D 2794-84. This test provides a further indication of coating adhesion and integrity on the panel substrate.

The results of the above tests are described in Table IV below. The results show that simple MDI-modification of D.E.N.™ 438 yields a resin with properties in the same, if not better, order as a CEN-based system in terms of adhesion and higher photospeed.

Table IV

TEST	Sample B Comparative Example (CEN-based)	Sample C Comparative Example (LEN-based)	Sample A (MDI-modified resin)
1	hard	soft	hard
2	50 after 5[1]	50 after 6[1]	50 after 4[1]
3	> 200	> 200	> 200
4	Minor peeling	peeling	NO peeling
5	124[2]	113[2]	149[2]

Notes:

1. survives X rubs after Y passes under exposure lamp
2. average of 3 measurements, value in inch. lbs.

CLAIMS:

1. An acrylated epoxy resin composition useful as an intermediate for a photocurable resin composition comprising the reaction product of:

(a) an epoxy adduct made by reacting

(i) an epoxy resin having two or more epoxides, and

(ii) a nitrogen-containing monomer compound; and

(b) an unsaturated carboxylic acid.

2. The composition of Claim 1 wherein the epoxy resin is an epoxy novolac resin.

3. The composition of Claim 1 wherein the nitrogen-containing compound is diphenylmethane diisocyanate.

4. The composition of Claim 1 wherein the nitrogen-containing compound is toluene diisocyanate.

5. The composition of Claim 1 wherein the nitrogen-containing compound is sulfanilamide.

6. The composition of Claim 1 wherein the nitrogen-containing compound is 2,6-dimethylcyclo-hexylamine.

7. A half-ester resin composition useful for a photocurable resin composition comprising the reaction product of:

(a) an acrylated epoxy resin of any one of Claims 1 to 6; and

(b) an anhydride compound.

8. The half-ester resin of Claim 7 wherein the anhydride is succinic anhydride.

9. The half-ester resin of Claim 7 wherein the anhydride is methylhexahydrophthalic anhydride.

10. A photocurable composition comprising the mixture of:

(a)a half-ester resin of Claim 7;

(b) a photoinitiator;

(c) a sensitizor;

(d) a hardener catalyst;

(e) a solid epoxy novolac resin; and

a reactive diluent.

11. A process for making an acrylated epoxy resin composition comprising reacting:

(a) an epoxy adduct made from reacting

(i) an epoxy resin having two or more epoxides, and

(ii) a nitrogen-containing monomer compound; and

(b) an unsaturated carboxylic acid.

12. A process for making a half-ester resin composition useful for a photocurable resin composition comprising reacting:

(a) an acrylated epoxy resin; and

(b) an anhydride compound.

13. A process for making a photocurable composition comprising mixing:

(a)a half-ester epoxy resin;

(b) a photoinitiator;

(c) a sensitizor;

(d) a hardener catalyst;

(e) a solid epoxy novolac resin; and

(f) a reactive diluent.

14. A cured coating for a substrate comprising the reaction product of (a) the photocurable composition of Claim 10 and (b) a curing source.

15. The coating of Claim 14 wherein the curing source is selected from ultra violet (UV) light, infrared light and heat.

INTERNATIONAL SEARCH REPORT

National Application No
PCT/US 98/07610

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G59/14

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 43 36 451 A (TILLER HANS JUERGEN ;HELBIG MANFRED DR (DE)) 27 April 1995 see page 3, line 16-27; claims 1,9; example 2 ---	1-6,11, 14,15
X	EP 0 587 189 A (NIPPON CATALYTIC CHEM IND) 16 March 1994 see page 5, line 36-42; claims ---	1-15
X	US 4 253 918 A (TRAENCKNER HANS-JOACHIM ET AL) 3 March 1981 see column 2, line 29-49; claims see column 3, line 35 - column 4, line 53 ---	1,2,5,6, 11,14,15
X	US 5 548 005 A (KURTH INGE ET AL) 20 August 1996 see claims --- -/--	1-6,11, 14,15

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 August 1998	20/08/1998

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INTERNATIONAL SEARCH REPORT

national Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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X	KLEE J ET AL: "SYNTHESIS AND INVESTIGATION OF A,W-METHACRYLOYL TERMINATED EPOXIDE-AMINE MACROMONOMERS" POLYMER BULLETIN, vol. 27, no. 5, 1 January 1992, pages 511-517, XP000259921 see page 511 - page 517	1
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/US 98/07610

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