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(54) Title: MODIFIED AMINOPLAST CROSSLINKERS

(57) Abstract: A crosslinking agent that is an ungelled reaction product of (a) at least one aminoplast resin and (b) at least one aromatic heterocycle containing at least one nitrogen atom wherein the crosslinking agent is essentially free of active hydrogen functional groups and has a glass transition temperature of at least 10°C is disclosed. Methods for preparing crosslinking agents are also disclosed. Further provided is a curable powder coating composition including a polymer having a glass transition temperature of at least 30°C containing reactive functional groups and the present crosslinking agent; a multilayer composite coating composition and substrates coated therewith are also disclosed.

MODIFIED AMINOPLAST CROSSLINKERS

5

FIELD OF THE INVENTION

The present invention relates to crosslinking agents based on modified aminoplast resins and to powder coating compositions containing these crosslinking agents.

10

BACKGROUND OF THE INVENTION

In recent years, powder coatings have become increasingly popular because these coatings are inherently low in volatile organic content ("VOC"). The low VOC significantly reduces air emissions into the atmosphere during application and curing as compared to liquid coatings.

15

Hydroxyl, carboxyl, carbamate, and/or epoxy functional resins, such as acrylic and polyester resins having relatively high glass transition temperatures ("Tg"), are commonly used as the main film-forming polymers for powder coatings. The relatively high Tg of such polymers provides powder coatings having good storage stability. When exposed to the extreme

20 temperatures both during shipping and/or storage, however, even better powder coating stability is desired. By "stability" or "storage stability" is meant the ability of the individual powder particles that comprise the powder coating to resist the tendency to adhere to one another, which causes "clumping" or "fusing" of the powder coating composition. Powder coating compositions

25 having very poor storage stability can be difficult, if not impossible, to apply.

30

Aminoplast resins are well known in the art as low cost crosslinking agents for hydroxyl, carboxyl, and/or carbamate functional polymers in conventional liquid coating compositions. Aminoplast resins can impart enhanced properties to the coatings, such as exterior durability, chemical

30 resistance, and mar resistance. Attempts to produce powder coating compositions based on conventional aminoplast resins that provide these desirable properties often give unsatisfactory results because these materials

are typically in liquid form. In addition to problems with incorporating the liquid aminoplast into the powder coating, their incorporation, when successful, can result in a coating having poor powder stability.

5 Methoxylated aldehyde condensates of glycoluril, which are solid aminoplast resins, are employed as crosslinking agents in powder coating compositions. Although solid in form, these materials can still depress the T_g of the powder coating composition significantly, even when combined with high T_g film-forming polymers such as the acrylic polymers discussed above. A depression in T_g can also result in poor powder stability.

10 Moreover, the use of conventional aminoplast resins in powder coating compositions can result in the phenomenon commonly referred to as "gassing". Gassing can occur as a result of vaporization of the alcohol generated in the thermally induced aminoplast crosslinking reaction. The alcohol vapor is driven off through the coating film upon heating; as the
15 viscosity of the coating increases during the curing process, "pinholes" or "craters" are formed as the gas escapes through the coating surface.

Thus, there is a need in the art for improved aminoplast crosslinkers that can be used with powder coatings.

20

SUMMARY OF THE INVENTION

The present invention is directed to a crosslinking agent comprising the ungelled reaction product of (a) at least one aminoplast resin; and (b) at least one aromatic heterocycle containing at least one nitrogen atom. A method for preparing such a crosslinking agent is also disclosed.

25 As discussed above, the incorporation of aminoplast resins into powder coatings has been difficult to achieve. The present invention overcomes these difficulties by providing modified aminoplasts that are in solid, ungelled form. An "ungelled" product is one that has a measurable intrinsic viscosity when dissolved in a suitable solvent; a gelled product, in contrast, is one
30 whose intrinsic viscosity when dissolved in a solvent is too high to measure. In addition, an ungelled product can be melted, solidified, and remelted. The

ungelled products of the present invention can therefore be incorporated into powder coatings and processed according to methods standard in the art. Significantly, powder coatings containing the present modified aminoplasts give good performance, have good stability and are easy to use.

5

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed a crosslinking agent comprising an ungelled reaction product of (a) at least one aminoplast resin and (b) at least one aromatic heterocycle containing at least one nitrogen atom. The crosslinking agent is substantially free of functional groups that are reactive with an aminoplast resin, and has a Tg of at least 10°C.

Aminoplast resins are based on the condensation product of an aldehyde with an amino- or amido-group containing compound. While the aldehyde employed is most often formaldehyde, other aldehydes such as acetaldehyde, crotonaldehyde, acrolein, benzaldehyde, furfural, and glyoxal can also be used. Amine/amide containing compounds include those derived from at least one of glycoluril, aminotriazine, or benzoguanamine. Such compounds include, for example, alkoxyalkyl derivatives of melamine, glycoluril, benzoguanamine, acetoguanamine, formoguanamine, spiroguanamine, and the like. Condensation products obtained from the reaction of alcohols and formaldehyde with melamine, urea or benzoguanamine are most common and most suitable for use in the present invention. Condensation products of other amines and amides can also be employed, for example, aldehyde condensates of triazines, diazines, triazoles, guanadines, guanamines, and alkyl- and aryl-substituted derivatives of such compounds, including alkyl- and aryl-substituted ureas and alkyl- and aryl-substituted melamines. Some examples of such compounds are N,N'-dimethyl urea, benzourea, dicyandiamide, formaguanamine, acetoguanamine, glycoluril, ammeline, 2-chloro-4,6-diamino-1,3,5-triazine, 6-methyl-2,4-diamino-1,3,5-triazine, 3,5-diaminotriazole, triaminopyrimidine, 2-mercapto-4,6-diaminopyrimidine, and 3,4,6-tris(ethylamino)-1,3,5 triazine.

Aminoplast resins typically contain methylol or other alkylol groups and, in most instances, at least a portion of these alkylol groups are etherified by a reaction with an alcohol. Any monohydric alcohol can be employed for this purpose, including such alcohols as methanol, ethanol, propanol, butanol, 5 pentanol, hexanol, cyclohexanol, heptanol, and others, as well as benzyl alcohol, and other aromatic alcohols, cyclic alcohols such as cyclohexanol, monoethers of glycols, and halogen-substituted or other substituted alcohols, such as 3-chloropropanol and butoxyethanol. Aminoplast resins that are substantially alkylated with methanol or butanol are particularly suitable for 10 use herein.

Nonlimiting examples of suitable aminotriazine compounds suitable for use in the present invention include alkoxyalkyl aminotriazines, such as (methoxymethyl)melamine-formaldehyde resin, for example CYMEL 300, CYMEL 303, RESIMENE 745, and RESIMENE 757; ethylated-methylated 15 benzoguanamine-formaldehyde resin, for example CYMEL 1123; and methylated-butylated melamine-formaldehyde resin, for example CYMEL 1135, CYMEL 1133, and CYMEL 1168. These products are commercially available from either Cytec Industries, Inc. (CYMEL) or Solutia, Inc. (RESIMENE).

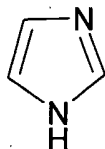
20 In another embodiment of the present invention, the aminoplast resin (a) comprises a compound derived from glycoluril, such as alkoxyated aldehyde condensates of glycoluril. The alkoxyated aldehyde condensates of glycoluril suitable for use as the aminoplast resin (a) can be prepared by reacting glycoluril, or acetylene diurea, with an aldehyde, typically 25 formaldehyde, to form tetra-alkylol glycoluril. In this embodiment, the alkylol groups are usually etherified with a mono-alcohol, such as a C₁ to C₆ mono-alcohol, to form tetra-alkoxy alkyl glycoluril. An example of such a tetra-alkoxyalkyl glycoluril is tetra-methoxy methyl glycoluril, which is commercially available as POWDERLINK 1174 from Cytec Industries, Inc.

30 In addition to the aminoplast resin (a), the reactants used to form the crosslinking agent of the present invention further comprise (b) at least one

aromatic heterocycle containing at least one nitrogen atom. An "aromatic heterocycle containing at least one nitrogen atom" refers to a compound comprising an aromatic ring or rings, fused or unfused, in which at least one member of the ring(s) is a nitrogen atom having an active hydrogen attached thereto. The aromatic ring(s) can contain more than one nitrogen, which may or may not have an active hydrogen attached thereto; the ring(s) can be substituted or unsubstituted. Any substituent that does not interfere with the reaction between the aminoplast resin and the aromatic heterocycle containing at least one nitrogen atom can be present, such as one or more monovalent hydrocarbon groups. A "monovalent hydrocarbon group" is an organic group containing carbon and hydrogen. These hydrocarbon groups may be aliphatic or aromatic, and may contain from 1 to 24 (in the case of aromatic from 3 to 24) carbon atoms. A "monovalent hydrocarbon group" can also be a heteroatomic hydrocarbon group; that is, one or more of the carbon molecules in the group can be substituted with heteroatoms, typically oxygen or nitrogen. Nonlimiting examples of such monovalent hydrocarbon groups include alkyl, alkoxy, aryl, alkylaryl and alkoxyaryl groups; substituents can be present on any of the molecules within the ring(s) so long as the active hydrogen attached to the nitrogen remains free for reaction with the aminoplast resin. Alkyl substituted compounds suitable for use in the present invention are widely commercially available.

Examples of suitable aromatic heterocycles containing at least one nitrogen atom include imidazoles, pyrazoles, triazoles, pyrroles and indoles.

Imidazoles have the general structure (I)

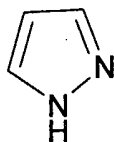


(I)

"Imidazole", "imidazole-containing", and like terms are used herein to describe compounds comprising a moiety depicted by structure (I), which moiety can

be substituted or unsubstituted, derivatized in any way or used in combination with other compounds.

Pyrazoles have the general structure (II)



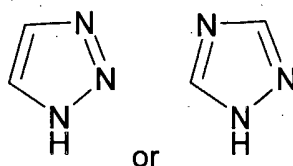
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(II)

"Pyrazole", "pyrazole-containing", and like terms are used herein to describe compounds comprising a moiety depicted by structure (II), which moiety can be substituted (II) or unsubstituted, derivatized in any way or used in combination with other compounds.

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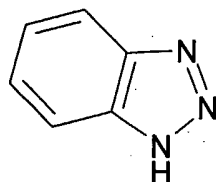
Triazoles have the general structure (III)



(III)

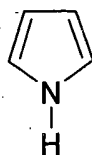
"Triazole", "triazole-containing" and like terms are used herein to describe compounds comprising a moiety depicted by structure (III), which moiety can be substituted (III) or unsubstituted, derivatized in any way or used in combination with other compounds. A particular class of derivatized triazoles are fused ring compounds such as benzotriazole (IIIa) and its derivatives.

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(IIIa)

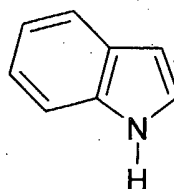
Pyrroles have the general structure (IV)



(IV)

"Pyrrole", "pyrrole-containing", and like terms are used herein to describe compounds comprising a moiety depicted by structure (IV), which moiety can be substituted (IV) or unsubstituted, derivatized in any way or used in combination with other compounds.

Indoles have the general structure (V)



(V)

"Indole", "indole-containing", and like terms are used herein to describe compounds comprising a moiety depicted by structure (V), which moiety can be substituted (V) or unsubstituted, derivatized in any way or used in combination with other compounds.

It will be appreciated that all of the compounds of Structures I through V have a nitrogen with an active hydrogen attached thereto. This moiety functions as a weak Bronsted acid. It will also be appreciated that these compounds are Lewis bases. In this respect, it was surprising that the present aromatic heterocycle compounds reacted with an aminoplast resin; because the reaction is normally catalyzed with a strong acid, a base would be expected to interfere with the catalyst and inhibit if not prohibit the reaction. No such inhibition occurs here.

The present crosslinkers can be prepared by further reaction with compound (c), as described below. In general, compound (c) is one which, when reacted with an aminoplast resin, will also form an ungelled crosslinking

agent. One or more of the compounds identified as compound (c) can be used. Suitable compounds include, for example:

5 a reactive polyhydric compound, such as one having two or more groups that are reactive toward the aminoplast including but not limited to diols and triols. Examples of suitable diols include but are not limited to cycloaliphatic diols such as hydrogenated Bisphenol A, cyclohexane dimethanol, cyclohexane diol and mixtures thereof. Examples of suitable triols include but are not limited to trimethylol propane, tris(hydroxyethyl) isocyanurate, and mixtures thereof;

10 a polyester polyol; any polyester having two or more reactive hydroxyl groups can be used, including but not limited to one comprising the condensation reaction product of a cycloaliphatic polyol and a cyclic polycarboxylic acid or anhydride. For example, the cycloaliphatic polyol can be any polyhydric cycloaliphatic compound known in the art including but not
15 limited to hydrogenated bisphenols such as Bisphenols A, F, E, M, P, Z and the like; cyclohexyl dimethanol, cyclohexane diol and mixtures thereof; the cyclic polycarboxylic acid/anhydride can be any cyclic compound having two or more carboxylic acid groups per molecule, including but not limited to hexahydrophthalic acid, phthalic acid, isophthalic acid, terephthalic acid,
20 anhydrides thereof and mixtures thereof;

a polyhydric aromatic compound, having one or more aromatic rings, fused or unfused, of which polyhydric phenols and dihydric aromatic compounds are examples;

25 a reactive urethane group such as one formed by the reaction of a polyester polyol and a monoisocyanate, or such as one formed from the reaction of a polyisocyanate and a monohydric capping agent; the polyester polyol can be any polyester having two or more reactive hydroxyl groups. Any isocyanate that is monofunctional with respect to the NCO group can be used; examples include but are not limited to cyclohexyl isocyanate, phenyl
30 isocyanate, butyl isocyanate and mixtures thereof. Similarly, any isocyanate having polyfunctionality can be used including but not limited to aliphatic

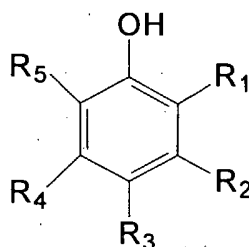
polyisocyanates, cycloaliphatic polyisocyanates, aromatic polyisocyanates, higher polyisocyanates and mixtures thereof. The monohydric capping agent can comprise a wide variety of mono-hydroxyl functional materials including but not limited to aliphatic alcohols, especially those having 1 to 6 carbons, and aromatic alcohols;

5 a monofunctional sulfonamide having only one active hydrogen, examples of which include but are not limited to saccharin and *N*-alkyl-*p*-toluene sulfonamide;

10 a carboxylic acid-containing compound, which is any compound that has at least one carboxylic acid functional group and has the appropriate acidity (i.e. a pKa of >3, such as >4). "pKa" values reported herein refer to pKa as measured in deionized water at 25°C. "pKa" will be understood as a means for expressing the strength of acids; the weaker the acid, the larger the pKa. If the pKa of the carboxylic acid-containing compound is below about 3, 15 the acid will catalyze the self-condensation of the aminoplast resin; this will result in a gelled rather than an ungelled reaction product. Similarly, the use of a polycarboxylic acid alone can result in a gelled product. Thus, the carboxylic acid-containing compound used in the present invention is most suitably a monofunctional acid, or a mixture of monofunctional and 20 polyfunctional acids. If such an acid mixture is used, the polyfunctional acid should typically comprise ≤ 20 percent of the mixture. Aromatic carboxylic acids, such as benzoic acid and its derivatives, are particularly suitable. Derivatives of benzoic acid include those materials having substitutions on the phenyl ring of the benzoic acid molecule; examples include toluic acid, anisic acid, and 4-*tert*-butylbenzoic acid. Aromatic group-containing alkyl carboxylic acids such as cinnamic acid and phenyl acetic acid and its derivatives are also suitable; derivatives of these acids include compounds where the phenyl ring of the acid is substituted. Other suitable monofunctional carboxylic acids include, but are not limited to, hexahydrobenzoic acid, diphenyl acetic acid 25 and those known to one skilled in the art. Polycarboxylic acids suitable for 30

use with one or more monofunctional carboxylic acids include, for example, phthalic acid, terephthalic acid, and trimellitic acid;

a monohydroxy aromatic compound having structure (VI):

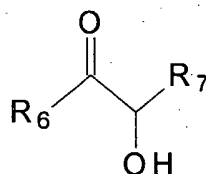


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(VI)

wherein each of R_1 through R_5 are the same or different and are selected from H, a monovalent hydrocarbon group, COOR_6 where R_6 is H or a monovalent hydrocarbon group, NO_2 , halogen or XR_7 , where X is oxygen or sulfur and R_7 is a monovalent hydrocarbon group having 1 to 8 carbon atoms; compounds having structure (VII):

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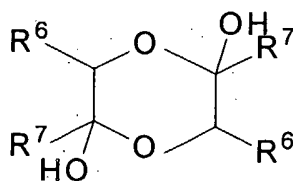


(VII)

or dimer derivatives thereof as discussed below, where R_6 and R_7 are the same or different and each independently represents an aromatic group having 4 to 20 carbons or an alkyl group having 1 to 12 carbon atoms. Suitable aromatic groups, include but are not limited to phenyl, naphthyl, methoxy phenyl, or dimethylaminophenyl groups, and can also contain one or more heteroatoms, such as O, N, and S, either internal or external to the aromatic ring; and

20

a compound having the general structure (VIII) which is the dimeric derivative of a compound having the general structure (VII).



(VIII)

Such dimer derivatives can have the structure (VIII) above where R⁶ and R⁷ are as described above for the structure (VII).

5 Some compounds referred to herein as "compound (c)" are described, for example, in U.S. Patent Nos. 4,254,235; 4,255,558; 4,393,181; 4,698,401; 6,451,928; 6,316,109; 6,441,103; 6,479,611; 6,500,545, all of which are hereby incorporated by reference. Again, mixtures of any of the above compounds identified as compound (c) can be used.

10 A particularly suitable embodiment is one wherein the aminoplast resin is reacted with at least one aromatic heterocycle containing at least one nitrogen atom and at least one carboxylic acid-containing compound, which can comprise one or more mono or polyfunctional acids. Inclusion of the carboxylic acid-containing compound as a reactant in the preparation of the crosslinking agent of the present invention can provide several advantages. First, reaction of the carboxylic acid-containing compound with the aromatic heterocycle containing at least one nitrogen atom and aminoplast resin can increase the T_g of the resulting crosslinker, as compared to a crosslinking agent formed with the aromatic heterocycle containing at least one nitrogen atom and aminoplast alone; this increase in T_g is achieved without any significant change in melt viscosity. Also, including a carboxylic acid-containing compound can allow for the reaction of more alkoxy groups of the aminoplast resin, which leads to formulations having less outgassing.

25 The aminoplast resin (a) generally constitutes 90 weight percent or less, often 85 weight percent or less, and typically 80 weight percent or less of the reaction mixture, based on the total combined weight of reactants (a), (b) and, if used, (c). Also, the aminoplast resin (a) generally constitutes at least 25 weight percent, often at least 35 weight percent, and typically at least 45

weight percent of the reaction mixture, based on the total combined weight reactants (a), (b) and, if used, (c). The percent by weight of the aminoplast resin (a) present in the reaction mixture can range between any combination of these values inclusive of the recited values.

5 The aromatic heterocycle containing at least one nitrogen atom compound (b) and, if used, compound (c), together generally constitute 75 weight percent or less, often 65 weight percent or less, and typically 55 weight percent or less of the reaction mixture, based on the total combined weight of reactants (a), (b) and, if used, (c). Also, the aromatic heterocycle containing
10 at least one nitrogen atom compound (b) and, if used, compound (c), together generally constitute at least 10 weight percent, often at least 15 weight percent, and typically at least 20 weight percent of the reaction mixture, based on the total combined weight of reactants (a), (b) and, if used, (c). The percent by weight of the aromatic heterocycle containing at least one nitrogen
15 atom compound (b) and, if used, compound (c) present in the reaction mixture can range between any combination of these values inclusive of the recited values.

 The crosslinking agents of the present invention generally have a Tg of at least 10°C, often at least 15°C, usually at least 20°C, and typically at least
20 25°C. Also, the crosslinking agent generally has a Tg of less than 85°C, often less than 80°C, usually less than 75°C, and typically less than 70°C. The Tg of the crosslinking agent can range between any combination of these values, inclusive of the recited values.

 The Tg can be measured experimentally using differential scanning
25 calorimetry (rate of heating 10°C per minute, Tg taken at the first inflection point). Unless otherwise indicated, the stated Tg as used herein refers to the measured Tg.

 The present invention is also directed to a method for preparing the present crosslinking agents. More specifically, the aminoplast resin (a) and
30 the aromatic heterocycle containing at least one nitrogen atom compound (b), either alone or in combination with one or more of compound (c), are

combined in a suitably equipped reaction vessel, typically with an appropriate strong acid as catalyst and optionally a suitable solvent. Any suitable solvent can be used, with aromatic solvents being most often employed. Examples of suitable aromatic solvents include xylene, toluene, and mixtures of these solvents. Examples of strong acids suitable for use as a catalyst include, but are not limited to, para-toluene sulfonic acid, dodecyl benzene sulfonic acid, and dodecyl benzene disulfonic acid. Normal condensation techniques well known in the art can be used. The reaction admixture is heated to a temperature ranging from 90°C to 160°C, usually from 100°C to 150°C, and held at that temperature for a period sufficient to obtain an ungelled product having a Tg of at least 10°C. The reaction is terminated when the reaction end point is detected by an appropriate analytical method(s). "An appropriate analytical method" will vary depending on the relevant active hydrogen-containing group(s). For example, an appropriate analytical method when OH and/or NH groups are involved would be the disappearance of the signal from these groups as determined by infrared spectra, and an appropriate analytical method for determining the disappearance of COOH groups would be to monitor acid number. An appropriate analytical method can be determined by one skilled in the art. Other suitable and/or equivalent methods for making the present crosslinkers can also be employed; for example compound(s) (c), if used, can be added after reaction of (a) and (b), or can be reacted separately with (a) and mixed with the reaction product of (a) and (b).

In the preparation of the crosslinking agent of the present invention, the aminoplast resin (a) and the aromatic heterocycle containing at least one nitrogen atom compound (b) are combined in a ratio such that the resulting reaction product is substantially free of active hydrogen-containing groups (specifically N-H groups and any other functional groups that may be incorporated through one or more of compound (c)). Any ratio of (a) to (b) that allows this result to be achieved is within the present invention. It has been found that particularly good crosslinkers (such as those having a Tg >25°C) are formed when the molar ratio of (a) and (b) is 1 to 2.5. (When the

aminoplast resin used is a mixture of compounds, the molecular weight is calculated based on the pure monomeric structure. For example, CYMEL 303 is treated as hexamethyl methanol melamine.) The reaction is monitored for the disappearance of the N-H functionality via infrared spectroscopy and is generally terminated when the product is free of the N-H functionality. In addition, when one or more of compound (c) is used, the reaction is monitored for the disappearance of the active hydrogen functionality via infrared spectroscopy or acid value measurement, depending on the active hydrogen-containing group(s) in compound (c). One aspect of the present methods is that the reaction between compounds (a) and (b) and optionally (c) is run to completion, i.e. until substantially all of compound (b) and compound (c), if used, is reacted with the aminoplast. The reaction is carried out under conditions so as to not promote or allow a significant amount (i.e. <5%) of self-condensation (methoxyl-methoxyl reactions) of the aminoplast.

The present invention is also directed to a curable powder coating composition comprising a solid particulate, film-forming mixture of (1) a polymer containing reactive functional groups, and (2) one or more of the crosslinking agents described above. The polymer (1) can be selected from a variety of polymers having aminoplast-reactive functional groups well known in the art, so long as the Tg of the polymer is sufficiently high to permit the formation of a stable, solid particulate composition. The Tg of the polymer (1) generally is at least 30°C, often at least 40°C, and typically at least 50°C. The Tg of the polymer (1) also generally is less than 130°C, often less than 100°C, and typically less than 80°C. The Tg of the functional group-containing polymer (1) can range between any combination of these values inclusive of the recited values.

Examples of polymers having reactive functional groups useful in the curable powder coating compositions of the invention include acrylic, polyester, polyurethane, polyepoxide, and polyether polymers. The polymer (1) typically comprises reactive functional groups selected from hydroxyl, epoxy, carboxyl and/or carbamate functional groups, or a combination thereof.

In one embodiment of the present invention, the polymer (1) comprises hydroxyl and/or carbamate functional groups. In another embodiment of the invention, the polymer (1) comprises epoxy and/or hydroxyl functional groups.

The functional group-containing polymer (1) generally is present in the curable powder coating compositions of the invention in an amount ranging from at least 5 percent by weight, often at least 20 percent by weight, typically at least 30 percent by weight, and usually at least 40 percent by weight based on the total weight of the powder coating composition. The functional group-containing polymer (1) also generally is present in the present powder coating compositions in an amount less than 95 percent by weight, often less than 90 percent by weight, typically less than 85 percent by weight, and usually less than 80 percent by weight based on the total weight of the powder coating composition. The amount of the functional group-containing polymer (1) in the powder coating compositions of the present invention can range between any combination of these values inclusive of the recited values.

The powder coating compositions of the present invention further comprise, as component (2), one or more of the crosslinking agents described above. The crosslinking agent (2) is generally present in an amount ranging from at least 2 percent by weight, often at least 10 percent by weight, typically at least 15 percent by weight, and usually at least 20 percent by weight based on the total weight of the powder coating composition. The crosslinking agent (2) also generally is present in an amount less than 95 percent by weight, often less than 80 percent by weight, typically less than 70 percent by weight, and usually less than 60 percent by weight based on the total weight of the powder coating composition. The amount of the crosslinking agent (2) present in the powder coating compositions of the present invention can range between any combination of these values inclusive of the recited values.

The components (1) and (2) of the curable powder coating composition may each independently comprise one or more functional species, and are each present in amounts sufficient to provide cured coatings having a

desirable combination of physical properties, e.g., smoothness, optical clarity, scratch resistance, solvent resistance and hardness.

As used herein, the term "reactive" refers to a functional group that forms a covalent bond with another functional group under suitable reaction
5 conditions.

As used herein, "cure" and like terms as used in connection with a composition, e.g., "a curable composition", shall mean that any crosslinkable components of the composition are at least partially crosslinked. In certain embodiments of the present invention, the crosslink density of the
10 crosslinkable components, i.e., the degree of crosslinking, ranges from 5 percent to 100 percent of complete crosslinking. In other embodiments, the crosslink density ranges from 35 percent to 85 percent of full crosslinking. In other embodiments, the crosslink density ranges from 50 percent to 85 percent of full crosslinking. One skilled in the art will understand that the
15 presence and degree of crosslinking, i.e., the crosslink density, can be determined by a variety of methods, such as dynamic mechanical thermal analysis (DMTA) using a Polymer Laboratories MK III DMTA analyzer conducted under nitrogen. This method determines the Tg and crosslink density of free films of coatings or polymers. These physical properties of a
20 cured material are related to the structure of the crosslinked network.

If desired, the powder coating compositions of the present invention can also include an adjuvant curing agent different from the crosslinking agent (2). The adjuvant curing agent can be any compound having functional groups reactive with the functional groups of the polymer (1) or the
25 crosslinking agent (2) described above. Nonlimiting examples of suitable adjuvant curing agents include blocked isocyanates, triazine compounds, conventional aminoplasts, glycoluril resins, and mixtures thereof; the use of these compounds is well known in the art.

A glycoluril resin particularly suitable for use as the adjuvant curing
30 agent is POWDERLINK 1174, commercially available from Cytec Industries, Inc. of Stamford, Connecticut.

When employed, the adjuvant curing agent generally is present in the powder coating compositions in an amount ranging from 5 to 10 percent by weight, often from 5 to 20 percent by weight, typically from 5 to 30 percent by weight, and usually from 5 to 50 percent by weight based on the total weight of the powder coating composition. When a triazine compound is used, it is typically present in the powder coating composition of the present invention in an amount ranging up to about 20 percent by weight, and usually from about 1 to 20 percent by weight, percent by weight being based on the total weight of the powder coating composition. Mixtures of the adjuvant curing agents can also be used advantageously.

Also, it should be understood that, for purposes of the present invention, the curable powder coating compositions that contain epoxy group-containing polymers typically also include an epoxide-reactive curing (i.e., crosslinking) agent, usually an acid functional curing agent, in addition to the aminoplast-based crosslinking agent (2). A secondary hydroxyl group can be generated upon reaction of each epoxy functional group with a functional group of the epoxide-reactive curing agent. These secondary hydroxyl groups are then available for further reaction with the aminoplast-based crosslinking agent (2). Suitable epoxide-reactive curing agents may have functional groups selected from the group consisting of hydroxyl, thiol, primary amines, secondary amines, acid (e.g. carboxylic acid), and mixtures thereof. Useful epoxide reactive curing agents having amine functionality include, for example, dicyandiamide and substituted dicyandiamides. Preferably, the epoxide reactive curing agent has carboxylic acid groups.

The powder coating compositions of the present invention can further include additives commonly known in the art. Typical additives include benzoin, used to reduce entrapped air or volatiles; flow aids or flow control agents, which aid in the formation of a smooth and/or glossy surface, for example, MODAFLOW available from Monsanto Chemical Co.; waxes such as MICROWAX C available from Hoechst; fillers such as calcium carbonate, barium sulfate and the like; pigments and dyes as colorants; UV light

stabilizers such as TINUVIN 123 or TINUVIN 900 available from CIBA Specialty Chemicals and catalysts to promote the various crosslinking reactions. Such additives are typically present in the powder coating compositions of the present invention in an amount ranging from 1 to 60
5 weight percent based on total weight of the powder coating composition.

The powder coating compositions of the invention can be prepared by any means known in the art, such as by blending the functional group-containing polymer (1) and the crosslinking agent (2) in a Henschel blade blender. The mixture is then usually extruded through a Baker-Perkins twin
10 screw extruder at a temperature ranging from 158°F to 266°F (70°C to 130°C). The resultant chip is usually ground and classified to an appropriate particle size, typically between 20 and 200 microns, in a cyclone grinder/sifter.

The powder coating compositions of the invention can be applied to a variety of substrates including metallic substrates, for example, aluminum and
15 steel substrates, and non-metallic substrates, for example, thermoplastic or thermoset composite substrates. The powder coating compositions are typically applied by spraying, and in the case of a metal substrate, by electrostatic spraying which is preferred, or by the use of a fluidized bed. The powder coating can be applied in a single sweep or in several passes to
20 provide a film having a thickness after cure of from about 1 to 10 mils (25 to 250 micrometers), usually about 2 to 4 mils (50 to 100 micrometers).

Generally, after application of the powder coating composition, the powder coated substrate is heated to a temperature sufficient to cure the coating, typically to a temperature ranging from 250°F to 500°F (121.1°C to
25 260.0°C) for 1 to 60 minutes, and preferably from 300°F to 400°F (148.9°C to 204.4°C) for 15 to 30 minutes.

The curable powder coating composition can be applied as a primer or primer surfacer, or as a top coat, for example, a "monocoat". In one
embodiment, the present invention is directed to a curable powder coating
30 composition that is advantageously employed as a top coat in a multi-layer composite coating composition. Such a multi-layer composite coating

composition generally comprises a film-forming base coat, which typically is deposited from a film-forming base coating (typically pigmented) composition, and a top coat applied over the base coat, the top coat being deposited from the curable powder coating composition of the present invention. In a particular embodiment, the multi-component composite coating composition is a color-plus-clear system where the top coat is deposited from a powder coating composition that is substantially pigment-free, i.e., a clear coat.

The film-forming composition from which the base coat is deposited can be any of the compositions useful in coatings applications, for example, in automotive applications where color-plus-clear systems are most often used. A film-forming composition conventionally comprises a resinous binder and often a pigment to serve as a colorant. Particularly useful resinous binders include acrylic polymers, polyesters including alkyds, and polyurethanes.

The resinous binders for the base coat can be organic solvent-based materials, such as those described in U.S. Patent No. 4,220,679. Water-based coating compositions, such as those described in U.S. Patent Nos. 4,403,003; 4,147,679; and 5,071,904, can also be used as the base coat composition.

As mentioned above, the base coat compositions also can contain pigments of various types as colorants. Suitable metallic pigments include aluminum flake, bronze flake, copper flake, and the like. Other examples of suitable pigments include mica, iron oxides, lead oxides, carbon black, titanium dioxide, talc, as well as a variety of color pigments.

Optional ingredients for the base coat film-forming compositions include those that are well known in the art of surface coatings and include surfactants, flow control agents, thixotropic agents, fillers, anti-gassing agents, organic co-solvents, catalysts, and other suitable adjuvants.

The base coat film-forming compositions can be applied to the substrate by any of the conventional coating techniques, such as brushing, spraying, dipping or flowing, but they are most often spray-applied. The usual

spray techniques and equipment for air spraying, airless spraying and electrostatic spraying can be used.

The base coat film-forming compositions are typically applied to the substrate so that a cured base coat will have a dry film thickness ranging from 0.5 to 4 mils (12.5 to 100 micrometers). After forming a film of the base coat on the substrate, the base coat can be cured or alternatively given a drying step in which solvent, i.e., organic solvent and/or water, is driven off by heating or an air drying step before application of the clear coat. Suitable drying conditions will depend on the particular base coat film-forming composition and on the ambient humidity with certain water-based compositions. In general, a drying time ranging from 1 to 15 minutes at a temperature of 75°F to 200°F (21°C to 93°C) is adequate.

The curable powder top coating composition can be applied over at least a portion of the base coat by any of the methods of application described above. The curable powder top coating composition can be applied to a cured base coat or a dried but uncured base coat. In the latter case, the top coat and the base coat are cured simultaneously.

As used herein, unless otherwise expressly specified, all numbers such as those expressing values, ranges, amounts or percentages may be read as if prefaced by the word "about", even if the term does not expressly appear. Also, any numerical range recited herein is intended to include all sub-ranges subsumed therein. Plural encompasses singular and vice versa. Also, while use of certain components of the present invention may be described in the singular in certain places, this should not be read as limiting the invention to the singular. For example, some portions of the specification may describe use of "a" compound (c), although the invention clearly encompasses use of one or more compounds identified as (c). As used herein, the term "polymer" refers to oligomers and both homopolymers and copolymers, and the prefix "poly" refers to two or more.

30

EXAMPLES

The following examples are intended to illustrate the invention, and should not be construed as limiting the invention in any way.

5

Example 1

Into a two-liter four-necked reaction kettle equipped with a thermometer, a mechanical stirrer, a nitrogen inlet, and means for removing the by-product (methanol) were placed 320.0 parts by weight of CYMEL 303 ((methoxymethyl)melamine-formaldehyde resin from Cytec Specialty
10 Chemicals, Inc.), 100.6 parts by weight of pyrazole (obtained from Acros), and 0.5 parts by weight of *p*-toluenesulfonic acid. The mixture was heated to 110°C and the temperature was maintained under a 1.0 CFH (cubic feet per hour) nitrogen sparge while the methanol by-product was removed from the system. The reaction progress was monitored by measuring the IR spectra of
15 the mixture and was terminated when the end point (no detectable N-H signal) was reached. The product was allowed to cool slightly and poured out from the reactor. The product thus obtained was a pale yellow solid with a softening temperature of around 15°C.

20

Example 2

Into a two-liter four-necked reaction kettle equipped with a thermometer, a mechanic stirrer, a nitrogen inlet, and means for removing the by-product (methanol) were placed 640.0 parts by weight of CYMEL 303,
412.8 parts by weight of 3,5-dimethyl-1H-pyrazole (obtained from Acros), and
25 1.0 part by weight of *p*-toluenesulfonic acid. The mixture was heated to 140°C and the temperature was maintained under a 1.0 CFH nitrogen sparge while the methanol by-product was removed from the system. The reaction progress was monitored by measuring the IR spectra of the mixture and was terminated when the end point (no detectable N-H signal) was reached. The
30 product was allowed to cool slightly and poured out from the reactor. The

product thus obtained was a pale yellow solid with a softening temperature of around 43°C.

Example 3

5 Into a two-liter four-necked reaction kettle equipped with a thermometer, a mechanic stirrer, a nitrogen inlet, and means for removing the by-product (methanol) were placed 640.0 parts by weight of CYMEL 303, 499.8 parts by weight of benzotriazole (obtained from PMC Specialty Group), and 1.0 part by weight of p-toluenesulfonic acid. The mixture was heated to
10 90°C and the temperature was maintained under a 1.0 CFH nitrogen sparge while the methanol by-product was removed from the system. The reaction progress was monitored by measuring the IR spectra of the mixture and was terminated when the end point (no detectable N-H signal) was reached. The product was allowed to cool slightly and poured out from the reactor. The
15 product thus obtained was a pale yellow solid with a softening temperature of around 33°C.

Example 4

 Into a two-liter four-necked reaction kettle equipped with a
20 thermometer, a mechanic stirrer, a nitrogen inlet, and means for removing the by-product (methanol) were placed 640.0 parts by weight of CYMEL 303, 276.0 parts by weight of 1,2,4-1H-triazole (obtained from DSM), and 1.0 part by weight of p-toluenesulfonic acid. The mixture was heated to 105°C and the temperature was maintained under a 1.0 CFH nitrogen sparge while the
25 methanol by-product was removed from the system. The reaction progress was monitored by measuring the IR spectra of the mixture and was terminated when the end point (no detectable N-H signal) was reached. The product was allowed to cool slightly and poured out from the reactor. The product thus obtained was a pale yellow solid with a softening temperature of
30 around 24°C.

Example 5

Into a two-liter four-necked reaction kettle equipped with a thermometer, a mechanic stirrer, a nitrogen inlet, and means for removing the by-product (methanol) were placed 640.0 parts by weight of CYMEL 303, 5 272.0 parts by weight of imidazole (obtained from Acros), and 1.0 part by weight of p-toluenesulfonic acid. The mixture was heated to 150°C and the temperature was maintained under a 1.0 CFH nitrogen sparge while the methanol by-product was removed from the system. The reaction progress was monitored by measuring the IR spectra of the mixture and was 10 terminated when the end point (no detectable N-H signal) was reached. The product was allowed to cool slightly and poured out from the reactor. The product thus obtained was a pale yellow solid with a softening temperature of around 18°C.

15

Example 6

Into a two-liter four-necked reaction kettle equipped with a thermometer, a mechanic stirrer, a nitrogen inlet, and means for removing the by-product (methanol) were placed 640.0 parts by weight of CYMEL 303, 328.0 parts by weight of 2-methyl imidazole (obtained from Acros), and 1.0 20 part by weight of p-toluenesulfonic acid. The mixture was heated to 155°C and the temperature was maintained under a 1.0 CFH nitrogen sparge while the methanol by-product was removed from the system. The reaction progress was monitored by measuring the IR spectra of the mixture and was terminated when the end point (no detectable N-H signal) was reached. The 25 product was allowed to cool slightly and poured out from the reactor. The product thus obtained was a pale yellow solid.

Example 7

Into a two-liter four-necked reaction kettle equipped with a 30 thermometer, a mechanic stirrer, a nitrogen inlet, and means for removing the by-product (methanol) were placed 640.0 parts by weight of CYMEL 303,

384.0 parts by weight of 2-ethyl imidazole (obtained from Acros), and 1.0 part by weight of p-toluenesulfonic acid. The mixture was heated to 155°C and the temperature was maintained under a 1.0 CFH nitrogen sparge while the methanol by-product was removed from the system. The reaction progress was monitored by measuring the IR spectra of the mixture and was terminated when the end point (no detectable N-H signal) was reached. The product was allowed to cool slightly and poured out from the reactor. The product thus obtained was a pale yellow solid.

10

Example 8

Into a two-liter four-necked reaction kettle equipped with a thermometer, a mechanic stirrer, a nitrogen inlet, and means for removing the by-product (methanol) were placed 488.0 parts by weight of CYMEL 303, 250.0 parts by weight of 4-methyl imidazole (obtained from Acros), and 1.0 part by weight of p-toluenesulfonic acid. The mixture was heated to 150°C and the temperature was maintained under a 1.0 CFH nitrogen sparge while the methanol by-product was removed from the system. The reaction progress was monitored by measuring the IR spectra of the mixture and was terminated when the end point (no detectable N-H signal) was reached. The product was allowed to cool slightly and poured out from the reactor. The product thus obtained was a pale yellow solid with a softening temperature of around 20°C.

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Example 9

Into a two-liter four-necked reaction kettle equipped with a thermometer, a mechanic stirrer, a nitrogen inlet, and means for removing the by-product (methanol) and applying vacuum were placed 640.0 parts by weight of CYMEL 303, 142.8 parts by weight of benzotriazole, 476.5 parts by weight of p-toluic acid (obtained from Wuhan Organic Chemical Company), and 0.9 part by weight of p-toluenesulfonic acid. The mixture was heated to 145°C and the temperature was maintained under -650 mm Hg vacuum while

25

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the methanol by-product was removed from the system. The reaction progress was monitored by sampling the mixture for acid value and was terminated when an acid value of less than 9 was detected. The product was allowed to cool slightly and poured out from the reactor. The product thus
5 obtained was a pale yellow solid with a Tg of 43°C.

The process was repeated, only using no benzotriazole. The product thus obtained was a pale yellow solid with a Tg of 32°C. This demonstrates that the combination of benzotriazole and carboxylic acid gave a higher Tg than carboxylic acid alone.

10

Example 10

Into a two-liter four-necked reaction kettle equipped with a thermometer, a mechanic stirrer, a nitrogen inlet, and means for removing the by-product (methanol) and applying vacuum were placed 640.0 parts by
15 weight of CYMEL 303, 119.0 parts by weight of benzotriazole, 571.8 parts by weight of p-toluic acid, and 0.9 part by weight of p-toluenesulfonic acid. The mixture was heated to 145°C and the temperature was maintained under -650 mm Hg vacuum while the methanol by-product was removed from the system. The reaction progress was monitored by sampling the mixture for acid value
20 and was terminated when an acid value of less than 15 was detected. The product was allowed to cool slightly and poured out from the reactor. The product thus obtained was a pale yellow solid with a Tg of 42°C.

The process was repeated, only using no benzotriazole. The product thus obtained was a pale yellow solid with a Tg of 32°C. This demonstrates
25 that the combination of benzotriazole and carboxylic acid gave a higher Tg than carboxylic acid alone.

Example 11

Into a two-liter four-necked reaction kettle equipped with a
30 thermometer, a mechanic stirrer, a nitrogen inlet, and means for removing the by-product (methanol) and applying vacuum were placed 640.0 parts by

weight of CYMEL 303, 261.8 parts by weight of benzotriazole, 340.4 parts by weight of p-toluic acid, and 0.9 part by weight of p-toluenesulfonic acid. The mixture was heated to 145°C and the temperature was maintained under -650 mm Hg vacuum while the methanol by-product was removed from the system.

5 The reaction progress was monitored by sampling the mixture for acid value and was terminated when an acid value of less than 9 was detected. The product was allowed to cool slightly and poured out from the reactor. The product thus obtained was a pale yellow solid with a Tg of 55°C.

The procedure was repeated, except while heating the mixture to

10 145°C and removing the methanol, the temperature was maintained under atmospheric pressure instead of under vacuum. The reaction progress was monitored by sampling the mixture for acid value and was terminated when an acid value of less than 9 was detected. The product was allowed to cool slightly and poured out from the reactor. The product thus obtained was a

15 pale yellow solid with a Tg of 54°C. The reaction carried out under vacuum proceeded more rapidly as compared to the one carried out under atmospheric pressure.

Example 12

20 Into a two-liter four-necked reaction kettle equipped with a thermometer, a mechanic stirrer, a nitrogen inlet, and means for removing the by-product (methanol) and applying vacuum were placed 640.0 parts by weight of CYMEL 303, 151.8 parts by weight of 1,2,4-1H-triazole, 340.4 parts by weight of p-toluic acid, and 0.9 part by weight of p-toluenesulfonic acid.

25 The mixture was heated to 145°C and the temperature was maintained under -650 mm.Hg vacuum while the methanol by-product was removed from the system. The reaction progress was monitored by sampling the mixture for acid value and was terminated when an acid value of less than 20 was detected. The product was allowed to cool slightly and poured out from the

30 reactor. The product thus obtained was a pale yellow solid with a Tg of 42°C.

Example 13

Samples 1 to 4 were prepared using the ingredients and amounts (in grams) shown in Table 1. The samples were prepared as follows. The ingredients were weighed together and processed for ~20s in a Prism blender at 3500 rpm's. This premix was then extruded through a b&p Process Equipment and Systems 19 mm co-rotating twin screw extruder at 450 rpm's at temperatures ranging from 100°C to 115°C. The resultant chip was milled and classified to a median particle size of 30 to 50 μm on a Hosokawa Micron Powder Systems Air Classifying Mill I. The formulas were then electrostatically sprayed using Nordson equipment onto cold rolled steel panels supplied by ACT Laboratories as B-1000 P60 DIW, nonpolished panels. Finally, the panels were baked in electric Despatch LAD series ovens over a 25 minute dwell time. Samples 1 and 2 were baked for 25 minutes at 385°F and Samples 3-5 for 25 minutes at 375°F. All testing was run at a dry film thickness of 2.0 to 3.0 mils.

Table 1

Material	Sample 1	Sample 2	Sample 3	Sample 4
URALAC P-5504 ¹	--	359.1	359.1	359.1
CRYLCOAT 290 ²	390.0	--	--	--
CYMEL 303	25.0	--	--	--
Product from Ex. 11 (vacuum method)	--	59.5	--	--
Product from Ex. 11 (no-vacuum)	--	--	70.0	--
Product from Ex. 12	--	--	--	59.5
Di- <i>p</i> -tolylsulfonimide	1.0	1.5	1.5	1.5
2,2,6,6-tetramethylpiperidinol	0.40	0.6	0.6	0.6
Benzoin	3.0	3.0	3.0	3.0
RESIFLOW PL-200 ³	6.0	6.0	6.0	6.0
LICOWAX ⁴	3.0	6.0	6.0	6.0
Thixcin R ⁵	--	20.0	20.0	20.0
Dibutylamine	--	0.6	0.6	0.6
POWDERMATE 542 DG ⁶	3.0	--	--	--
TiO ₂ R706	235.0	220.0	220.0	220.0
Powder Stability 1 day @ 40°C ⁷	Fused	Cakey	Cakey	Excellent
Powder Stability 7 day @ 40°C	Sintered	Clumpy	Fused	Fused
Impact (direct/reverse)(in-lbs) ⁸	40/50	70/60	160/160	90/40
MEK (50 double rubs) ⁹	2	4	3	3
Off-gassing thickness (mils) ¹⁰	<2	9.3-9.7	7.2-7.6	7.5-8.3

¹ Standard durable 40 OH functional polyester, from DSM Resins.

² Standard durable 30 OH functional polyester from UCB Chemicals.

³ Acrylic flow additive dispersed on silica, from Estron Chemical.

⁴ Ethylene bis(stearamide), from Clariant Additives.

⁵ Castorwax derivative, from Elementis Specialties.

⁶ Proprietary degassing agent, from Troy Corporation.

⁷ Powder stability was tested by filling a 2 oz. glass jar half full of powder, sealing it, and placing it into a controlled temperature water bath at the designated temperature for a specified amount of time. At the completion of the testing, the sample was allowed to rest outside of the bath for 30 minutes. The jar was then rapped upside down on a hard surface 2 to 3 times and the condition of the powder was rated as follows: Excellent>Good>Slightly Cakey>Cakey>Slight Clumpy>Clumpy>Fused>Sintered.

⁸ Impact testing was run according to ASTM D 2794 using a Byk-Gardner Falling Dart Impact tester.

⁹ MEK resistance was run by rubbing a Q-tip soaked with methyl ethyl ketone back and forth across a panel (one double rub) 50 times and then rating the resulting marks as follows: MEK rating system:

- 5
- 0 No change
 - 1 Slight gloss loss around test area
 - 2 Barely detectable gloss loss in test area
 - 3 Barely detectable scuffing of test area
 - 10 4 Slightly detectable scuffing of test area
 - 5 Noticeable scuffing of test area
 - 6 Marring of test area
 - 7 Smearing of test area

Readings of 0-5 are generally regarded as acceptable.

15 ¹⁰ Off-gassing was tested by spraying a panel so that the coating increased in thickness from top to bottom. The panel was baked at 350°F for 25 minutes and the film thickness where pinholes and/or blisters began was recorded in mils. The higher the number, the more tolerant the coating is to off-gassing. The error in the test is approximately ± 1 mil.

20 As can be seen from the results of Table 1, the samples of the present invention, (Samples 2-4) provided had greatly enhanced stability and performance as compared to a powder coating using a standard melamine resin.

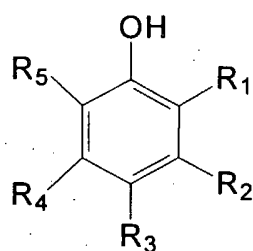
25 Whereas particular embodiments of this invention have been described above for purposes of illustration, it will be evident to those skilled in the art that numerous variations of the details of the present invention may be made without departing from the invention as defined in the appended claims.

30

THEREFORE WE CLAIM:

1. A crosslinking agent comprising an ungelled reaction product of the following reactants:
 - 5 (a) at least one aminoplast resin; and
 - (b) at least one aromatic heterocycle containing at least one nitrogen atom;wherein the crosslinking agent has a glass transition temperature of at least 10°C and is substantially free of active hydrogen-containing groups.
- 10 2. The crosslinking agent of Claim 1, wherein (a) is or is derived from glycoluril, aminotriazine, or benzoguanamine.
3. The crosslinking agent of Claim 2, wherein the aminoplast resin
15 comprises an aminotriazine compound.
4. The crosslinking agent of Claim 3, wherein the aminotriazine compound comprises an (alkoxyalkyl) aminotriazine having one or less non-alkylated NH bond per triazine ring.
- 20 5. The crosslinking agent of Claim 4, wherein the (alkoxyalkyl) aminotriazine compound comprises a (methoxymethyl) aminotriazine compound.
- 25 6. The crosslinking agent of Claim 2, wherein (a) comprises an alkoxyated aldehyde condensate of glycoluril.
7. The crosslinking agent of Claim 6, wherein the alkoxyated aldehyde condensate of glycoluril comprises tetramethoxy methylglycoluril.
- 30 8. The crosslinking agent of Claim 1, wherein (b) comprises imidazole.

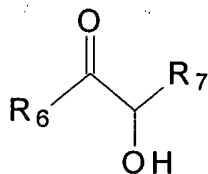
9. The crosslinking agent of Claim 1, wherein (b) comprises pyrazole.
10. The crosslinking agent of Claim 9, wherein (b) comprises dimethyl
5 pyrazole.
11. The crosslinking agent of Claim 1, wherein (b) comprises triazole.
12. The crosslinking agent of Claim 11, wherein (b) comprises
10 benzotriazole.
13. The crosslinking agent of Claim 1, wherein (b) comprises pyrrole.
14. The crosslinking agent of Claim 1, wherein (b) comprises indole.
15
15. The crosslinking agent of Claim 1, wherein said reaction product further
comprises:
- (c) one or more compounds selected from:
 - i) a reactive polyhydric compound;
 - 20 ii) a polyester polyol;
 - iii) a polyhydric aromatic compound;
 - iv) a reactive urethane group;
 - v) a monofunctional sulfonamide having only one active
hydrogen;
 - 25 vi) a polyhydric phenol; and
 - vii) a carboxylic acid-containing compound;
 - (viii) a monohydroxy aromatic compound having structure (VI):



(VI)

wherein each of R₁ through R₅ are the same or different and are selected from H, a monovalent hydrocarbon group, COOR₆ where R₆ is H or a monovalent hydrocarbon group, NO₂, halogen or XR₇, where X is oxygen and sulfur and R₇ is a monovalent hydrocarbon group having 1 to 8 carbon atoms; and

(ix) compounds having the following structure (VII):



(VII)

or dimer derivatives thereof, where R⁶ and R⁷ are the same or different and each independently represents an aromatic group or an alkyl group having 1 to 12 carbon atoms.

15 16. The crosslinking agent of Claim 15, wherein (c) comprises a carboxylic acid-containing compound.

17. The crosslinking agent of Claim 16, wherein (b) comprises triazole.

20 18. The crosslinking agent of Claim 17, wherein (b) comprises benzotriazole and (c) comprises toluic acid.

19. A method for modifying an aminoplast comprising:
- (a) mixing together:
 - (i) at least one aminoplast resin;
 - (ii) at least one aromatic heterocycle containing at least one
5 nitrogen atom;
 - (b) heating the admixture of step (a) to a temperature ranging from 90°C to 160°C; and
 - (c) maintaining the temperature achieved in step (b) for a time
sufficient to obtain an ungelled reaction product that has a glass
10 transition temperature of at least 10°C and that is essentially free of
active hydrogen-containing groups.
20. A curable powder coating composition comprising a solid particulate
film-forming mixture of the following components:
- 15 (1) at least one polymer containing reactive functional groups, said
polymer having a glass transition temperature of at least 30°C; and
 - (2) at least one crosslinking agent of Claim 1.
21. A multilayer composite coating composition comprising a base coat
20 deposited from a film-forming coating base coating composition and a top
coat over at least a portion of the base coat deposited from the curable
powder coating composition of Claim 20.
22. A substrate coated with the powder coating composition of Claim 20.
25
23. A substrate coated with the multilayer composite coating composition
of Claim 21.

24. A method for converting a liquid aminoplast into an ungelled crosslinking agent comprising:
- (a) mixing together:
 - (i) at least one aminoplast resin; and
 - 5 (ii) at least one aromatic heterocycle containing at least one nitrogen atom;
 - (b) heating the admixture of step (a) to a temperature ranging from 90°C to 160°C; and
 - (c) maintaining the temperature achieved in step (b) for a time
10 sufficient to obtain an ungelled reaction product that has a glass transition temperature of at least 10°C and that is essentially free of reactive active hydrogen-containing groups.
25. The method of Claim 24, wherein the aminoplast resin comprises a
15 (methoxymethyl)aminotriazine compound.
26. The method of Claim 24, wherein the aromatic heterocycle containing at least one nitrogen atom comprises imidazole.
- 20 27. The method of Claim 24, wherein the aromatic heterocycle containing at least one nitrogen atom comprises pyrazole.
28. The method of Claim 24, wherein the aromatic heterocycle containing at least one nitrogen atom comprises triazole.
25
29. The method of Claim 28, wherein the aromatic heterocycle containing at least one nitrogen atom comprises benzotriazole.
30. The method of Claim 28, wherein the aromatic heterocycle containing
30 at least one nitrogen atom comprises pyrrole.

31. The method of Claim 28, wherein the aromatic heterocycle containing at least one nitrogen atom comprises indole.

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INTERNATIONAL SEARCH REPORT

International Application No
/US2004/013953

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G12/40 C08L61/32 C08G12/26 C08G12/32 C09D161/32

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 7 C08G C08L C09D

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)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/033961 A1 (CHASSER ANTHONY M ET AL) 20 February 2003 (2003-02-20) page 2, paragraphs 14,17,18 page 5, paragraph 45 -----	1-31
X	US 5 665 852 A (SINGH BALWANT ET AL) 9 September 1997 (1997-09-09) column 2, line 25 - line 49 column 4, line 34 - line 47 column 5, line 8 - line 50 -----	1-31
X	EP 0 604 980 A (AMERICAN CYANAMID CO) 6 July 1994 (1994-07-06) example 1 -----	1-31
X	US 4 262 033 A (MASSY DEREK J R ET AL) 14 April 1981 (1981-04-14) column 2, line 17 - line 56 column 4, line 15 - line 20 -----	1-31

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

18 October 2004

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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