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(54) Title: REACTIVE NON-ISOCYANATE COATING COMPOSITIONS

(57) **Abrégé/Abstract:**

The invention pertains to a reactive, non-isocyanate coating compositions prepared by mixing epoxy, tertiary amine-, anhydride-, hydroxy- and, optionally, acid-functional compounds, a system of making the coating composition, and a substrate coated with the composition.

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REACTIVE NON-ISOCYANATE COATING COMPOSITIONS

The invention relates to reactive non-isocyanate coating compositions having mixtures of compounds containing 1) tertiary-amine, 2) anhydride, 3) epoxy, 5 4) hydroxy- and, optionally, 5) acid-functionalities. The invention further pertains to a coating system and to substrates coated with said coating compositions.

BACKGROUND OF THE INVENTION

Polymers that are used as binders in the preparation of coatings 10 compositions usually require that a cross-linking reaction occurs after the application of the composition. This cross-linking reaction is necessary to obtain desired properties such as mechanical strength, resistance against chemical agents, exterior durability, etc.

The cross-linking is often the result of the reaction between functional groups on 15 the polymer and co-reactive functional groups on a cross-linker added to the composition. Examples are the reaction between the hydroxyl groups of a polymer and melamine-formaldehyde resins or between hydroxyl groups and polyisocyanate resins.

20 High performance, low temperature curing polyurethane or polyurea coatings include reactive polyisocyanates and active hydrogen-containing compounds such as hydroxy-containing polymers or amine-containing polymers. Although these materials exhibit excellent performance and cure at low temperatures, the isocyanates may, under some conditions, be relatively 25 hazardous to handle.

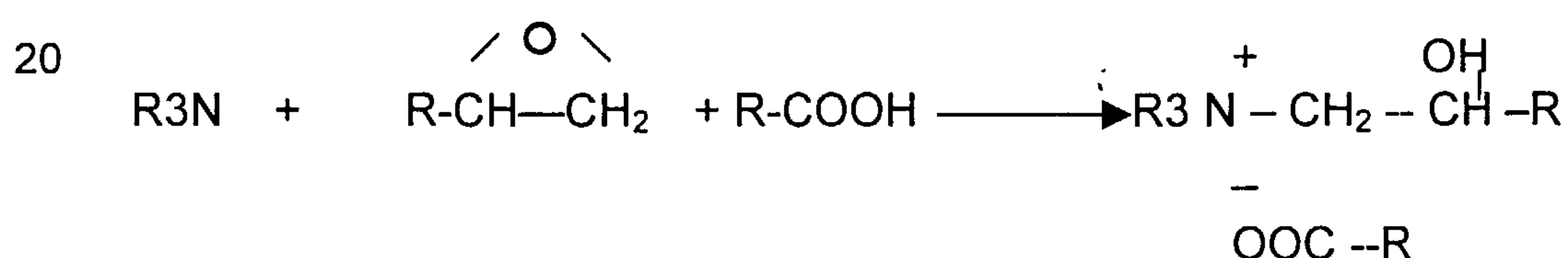
The coatings industry has been trying for years to develop non-isocyanate coating systems without sacrificing performance. Various non-isocyanate systems

developed suffer from inferior performance in one or more areas such as durability, gloss retention, drying, hardness, solvent and humidity resistance and the like.

The market interest for non-isocyanate coatings is driven by environmental
5 and safety concerns. Lower volatile organic compounds (VOC) and higher performance continue to be the driving forces for developing new and innovative coatings systems.

A non-isocyanate reactive coatings system, identified as the AA (All Acrylic)
10 System, is available from Akzo Nobel Resins, a part of Akzo Nobel. This AA system is composed of two functional compounds: the first compound is a polymer containing epoxy and hydroxy-functionalities and the second compound is a polymer having tertiary amine- and acid-functionalities. The epoxy and tertiary-amine groups are the dominant functionalities in these polymers.

15 The first major cure reaction in AA is the reaction of tert-amine with the epoxy group to form a quaternary ammonium ion with the aid of carboxylic acid:



25 Once the acid groups are consumed by the formation of quaternary ammonium ions, other reactions take place to consume the excess epoxy groups. For a description of the chemistry of "all acrylic" coatings see Leo G.J. Van de Ven, Rene T.M. Leijzer, Egbert Brinkman, and Paul Vandevoorde, Double Liasion, "Curing Mechanism of Waterborne Isocyanate Free All-Acrylic coatings", No. 498-499, pp.
30 67-71 (1997); also see: Proceeding Eurocoat 97, Sept. 23-25, pp.549-560 (1997) and Farbe Lack, Vol. 105, No. 8, pp. 24-28 (1999),; E.Brinkman, and Paul

Vandevoorde, "Waterborne two-pack isocyanate-free systems for industrial coatings", Progress in Organic Coatings 34, pp. 21-25 (1998); E.Manning and E.Brinkman, "All acrylic technology as an alternative to isocyanate-free polyurethane systems", Polymers Paint Colour, J. Vol. 190, No. 4426, pp. 21-23, 5 (2000); Richard Hall and Maarten Weber, "Waterborne All Acrylic (WBAA) Coatings in Transport and its Structure", Eurocoat, 2001, Lyon France.

The early hardness development (performance during the first few days), the ultimate flexibility, and solvent resistance of this system are unsatisfactory for 10 applications in metal coatings, such as for small machinery, agricultural implements and construction equipment. Improved performance properties are desired. The present invention addresses these weaknesses.

Other non-isocyanate systems comprise various combinations of anhydride, 15 hydroxy, epoxy, and acid compounds. These formulations utilize tertiary-amine as a catalyst for the anhydride-hydroxyl reaction. The tertiary-amine catalyst does not contribute to the crosslinked structure of the film network. These systems have poor chemical resistance, hydrolytic instability and poor exterior durability.

20 The following patents are a few examples of the prior art where catalytic amounts of tertiary amines are used to catalyze the anhydride-hydroxyl reaction. US Patent No. 4,732,790 describes a process of coating where one of the compositions applied is a high solids coating based on hydroxy-functional epoxies and anhydride. US Patent No. 4,452,948 describes a two-pack coating system 25 comprised of a hydroxyl component, an anhydride component and a catalyst. US Patent No. 4,871,806 refers to formulations of curable compositions comprising an acid-functional compound, an anhydride-functional compound, an epoxy-functional compound, and a hydroxy-functional compound. US Patent No. 5,227,243 refers to a substrate coated with a composition including a hydroxy-functional compound, an

anhydride-functional compound and cycloaliphatic epoxy compound. US Patent Nos. 4,826,921, 4,946,744, and 4,798,745 refer to the formulation of compositions including anhydride and hydroxy-functional compounds. US Patent No. 5,602,274 refers to the use of non-cyclic anhydride with other co-reactants such as, polyols, amines and epoxies. None of the prior art describes mixtures of compounds containing four (4) or five (5) functionalities in which a polymeric tertiary amine is used as co-reactant.

SUMMARY OF THE INVENTION

The invention relates to reactive, non-isocyanate coating compositions prepared by mixing epoxy-, tertiary amine-, anhydride-, hydroxy-and, optionally, acid-functional compounds, a method of coating the composition on a substrate and a substrate coated with the composition.

Thus in one aspect of the invention there is provided a reactive non-isocyanate coating composition obtained by mixing epoxy, tertiary amine, anhydride, hydroxy- and, optionally, acid-functional compounds, wherein: the tertiary amine-functional compound is an oligomeric or polymeric tertiary amine, with or without other functional groups, and is present in an amount greater than 0.5 mole %, the tertiary amine-functional groups are reactive with the epoxy-functional groups of the epoxy-functional compound, and the anhydride-functional compound is a monomeric, oligomeric or polymeric cyclic anhydride.

In a particular embodiment the coating composition further comprises an acid-functional compound.

In another aspect of the invention there is provided a coating system having at least three components which are combined to make a coating composition comprising: a component 1 being an oligomeric or polymeric tertiary amine-functional compound, a component 2 being a monomeric, oligomeric, or polymeric anhydride-functional compound, a component 3 being an oligomeric or polymeric epoxy-functional compound, and, the system also comprising a component 4 being a hydroxy-functional compound, the hydroxy-functional

4a

compound being a separate component or being combined with the oligomeric or polymeric tertiary amine-functional compound 1 or the epoxy-functional compound 2.

In a particular embodiment the coating system of the invention further comprises: a component 5 being an acid-functional compound, the acid-functional compound being a separate component or being combined with the oligomeric or polymeric tertiary amine-functional compound 1, the anhydride-functional compound 2, or the hydroxy-functional compound 4.

In still another aspect of the invention there is provided a substrate coated with the coating composition of of the invention, or with a coating composition made from the coating system of of the invention.

DETAILED DESCRIPTION OF THE INVENTION :

The composition of the invention includes a mixture of compounds such that the following functional groups are present therein: 1) tertiary-amine, 2) anhydride, 3) epoxy, 4) hydroxy, and optionally 5) acid. Each of these functionalities is co- reactant in the inventive composition. These functionalities can each be in individual compounds, which are combined to form the composition or two or more of them can be present on a polymer. For example, there can be three separate compounds with each compound having one or more functionality, or five separate compounds, each having one of the functionalities.

The components of the coating composition of the present invention can be packaged separately to provide shelf-stability and mixed together prior to the coatings application. One or more functional-compound (s) can be packaged. As an example, the anhydride, the amine and the epoxy compounds can be packaged

separately in three separate containers. According to this example, one of the components contains the hydroxy, the acid and/or the amine-functionalities which can be packaged together as a mixture of two or three separate compounds or as one copolymer containing all the three functionalities on the same copolymer. One
5 of the other components includes the epoxy and optionally the hydroxy-functionalities which can be packaged together as a mixture of two compounds each having a single functionality or as a single copolymer having two functionalities. Another component or package includes the anhydride-functionality, which can be packaged by itself or with the acid-functionality as a single copolymer
10 having the two functionalities or as a physical blend of two separate compounds. Due to its reactivity, the system has a limited pot-life (which is the useable time in which the composition can be applied) and should be used within the useful pot-life.

15 The tertiary amine-, epoxy- and hydroxy-functional group-containing compounds are polymers or oligomers with two or more, preferably three or more, functional groups in the molecule. Such multifunctional molecules are needed as a film former and to enable the formation of a polymeric, three-dimensional network. The anhydride and acid-functional group-containing compounds can be monomeric
20 and/or polymeric with one or more functional groups in the molecule. Preferably, the anhydride-functional group-containing compound is polymeric. The hydroxy-functionality can be introduced to the reactive system as part of the epoxy-, tertiary amine- and/or the acid-functional group-containing compounds and/or as separate hydroxy-functional polymers. Similarly, the acid-functionality can be introduced as
25 part of the anhydride, tertiary-amine and/or the hydroxy compounds and/or as separate acid-functional compounds. The reactive non-isocyanate coating compositions of the present invention provide high performance and low VOC industrial coatings with superior performance and excellent durability. These coatings are especially useful for finishing metal, plastic and wood articles.

More than one functionality can exist on the backbone of the same polymer, oligomer, or low molecular weight compound. Additionally, more than one functionality can be present in a component or package. The following combinations are disclosed by way of non-limiting examples:

- 5 Epoxy & Hydroxy
- Hydroxy & acid
- Hydroxy & amine
- Acid & amine
- Anhydride & acid
- 10 Acid, amine & hydroxy

The coating compositions of the present invention have a solvent system as a carrier. This carrier can be either water or organic solvent. The solvent can be a separate component or package, or it can be packaged together with one of the
15 other components. Stable water-borne or solvent-borne anhydride-, hydroxy-, epoxy-, amine- and, optionally, acid-functional compounds can be made and used in the present invention. If the composition is waterborne, emulsion polymerization of the monomers in the presence of a surface-active material and an initiator that generates free radicals in water is a convenient preparation method. Alternatively,
20 the copolymer can be prepared in an organic solution and subsequently emulsified in water.

Anhydride containing coatings systems are known for their fast early cure properties, but their overall properties are poor. It would not be thought desirable to
25 add an anhydride to the reactive non-isocyanate coating composition of the present invention, since one would think that the polymeric amine and polymeric anhydride would gel, forming a salt and making application, such as spraying, difficult. Additionally, it would be difficult to think of preparing and using anhydride-functional polymer in water due to the known instability of anhydride in aqueous

medium. However, the current invention clearly demonstrates that a fraction of the anhydride compound, monomer and/or polymer, can be hydrolyzed, neutralized with a base, and used as an ionic surfactant to self-emulsify the remainder of the anhydride compound. The hydrolyzed and neutralized fraction of the anhydride
5 constitutes the shell of the dispersed particle while the core contains the intact anhydride groups.

Conventional emulsification and dispersing approaches can be used to prepare the waterborne compounds used in the present invention. These include
10 the use of ionic and non-ionic surfactants in the emulsion polymerization of acrylic monomers containing epoxy- and/or hydroxy-functional groups. Acid-functional acrylic monomers such as 2-acrylamido, 2-methylpropane sulfonic acid and methoxypolyethylene glycol methacrylate can be used to render water dispersability for the anhydride and amine polymers.

15 The polymeric tertiary amine functions as a co-reactant in the inventive reactive non-isocyanate coating compositions, in addition to its catalytic function for the anhydride-hydroxyl reaction. The reactive system containing hydroxy, anhydride, tert-amine, epoxy, and optionally, acid groups give superior coatings
20 properties compared to the previously known non-isocyanate coatings systems. The anhydride and polymeric hydroxy react to form a hard initial network, which contributes to initial hardness and ultimate solvent resistance. The tertiary amine-functionality reacts with the epoxy-functionality and/or acid-functionality to generate quaternary ammonium and/or ammonium ions where ionic cross-links are formed
25 in addition to the covalent ester cross-links generated from the acid/epoxy reaction. The ionic cross-links allow for the delocalization of the lone pairs of electrons on the nitrogen atoms to give stable and durable network systems.

The equivalent ratios of various components that can be employed in the present invention are described in reference to the tertiary amine-functionality: for every one mole of tertiary amine used, there will be about 0.3 to about 75 moles of epoxy groups, about 0.05 to about 50 moles of anhydride groups, about 0.05 to
5 about 50 moles of hydroxy groups, and about 0.0 to about 10 moles of carboxyl groups. However, the preferred compositions include about 0.75 to about 10 moles of epoxy, about 0.1 to about 7 moles of anhydride groups, about 0.05 to about 7 moles of hydroxy groups, and about 0.0 to about 1 mole of carboxyl for every one mole of tertiary amine. Yet more preferred compositions of the present invention
10 include about 0.75 to about 5 moles of epoxy, about 0.1 to about 3 moles of anhydride groups, about 0.1 to about 3 moles of hydroxy groups, and about 0.0 to about 0.2 mole of carboxyl for every one mole of tertiary amine.

In certain compositions of the more preferred compositions where ambient
15 or low bake conditions are used, the epoxy and amine constitute the major components of the reactive non-isocyanate coating composition, while the anhydride, hydroxy, and optional acid are the minor components. For example, the molar ratio of the epoxy, amine, anhydride, hydroxy and optionally carboxyl functionalities can be 1.4/1/0.4-0.8/0.4-0.8/0.0-0.2, respectively.

20

However, higher amounts of the anhydride, hydroxy and optional acid can be practiced according to the present invention with great success in certain applications, especially at higher bake end-use applications. For this application, the molar ratio of the epoxy, amine, anhydride, hydroxy, and optionally carboxyl
25 functionalities can be, for example, 75/1/50/50/0.0-0.2, respectively.

The tertiary amine compound is a polymer which preferably has at least two or more tertiary amine groups per molecule. The average tertiary-amine equivalent weight can range, for example, from about 50 to about 3000. The anhydride

compound is a cyclic anhydride of di-carboxylic acids, which can be a monomer and/or a polymer with two or more anhydride-functionalities per molecule. The average anhydride equivalent weight can be, for example, as low as about 100 or as high as about 2000. The hydroxy compound is a polymer with at least two or
5 more functional groups per molecule. The average hydroxy equivalent weight can be, for example, as low as about 31 or as high as about 2000.

The compositions of the present invention can include any polymeric tertiary amine regardless of the backbone. Various backbone polymers include polyesters,
10 polyethers, acrylics, polyurethanes, or hydrocarbon type polymers. One method for the preparation of the acrylic polymeric tertiary amines is based on polymerizing an ethylenically unsaturated mono-tertiary-amine monomer with one or more other ethylenically unsaturated monomer(s) copolymerizable with the ethylenically unsaturated mono-tertiary-amine monomer. Examples of the ethylenically
15 unsaturated mono-tertiary-amine monomer include dimethylaminoethyl methacrylate or acrylate, diethylaminoethyl methacrylate or acrylate, dialkylaminoalkyl methacrylamide or acrylamide. Examples of the ethylenically unsaturated monomer(s) copolymerizable with the ethylenically unsaturated mono-tertiary-amine monomer include non-functional and optionally functional
20 ethylenically unsaturated monomers. Examples of the non-functional ethylenically unsaturated monomers include styrene, alpha-methyl styrene, alkyl acrylate and/or methacrylate having 1-18 carbons where the alkyl group is a linear or branched alkyl radical such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, dodecyl, 2-ethylhexyl, cyclohexyl, etc. The functional monomers include acid-
25 functional monomers and / or hydroxy-functional monomers. These acid and hydroxy-functional monomers are described under the corresponding sections of functional compounds.

Other types of tertiary-amine-functional polymers are those described below for the preparation of hydroxy-functional compounds from secondary amines and epoxides to produce hydroxy-and tertiary amine-functional polymers. The tertiary amine polymer is a co-reactant as well as a catalyst, so it contributes to the crosslinked structure of the film network. The contribution of the tertiary amine polymer to the network structure has not heretofore been the case in the presence of anhydride. The tertiary amine polymer has a major impact on the overall cross- linking and three-dimensional network formation as it forms polymeric salt and quaternary ammonium ions. It may be present at a level higher than a catalytic amount (higher than 0.5%). The polymer reacts in more than one site, which results in multiple cross-links. Generally, the polymeric tertiary amine is present at 0.5-60 mole %, and preferably above the 3 mole % level.

The hydroxy group-containing compound can be polymeric, e. g. hydroxy-functional polymer, such as hydroxy group-containing acrylic or polyester resin. Alternatively, the hydroxy group-containing compound can be incorporated into the epoxy, the acid or the amine polymers. Similarly, the acid groups can be introduced to the system as an acid-functional polymer (or monomer) or it can be incorporated along the backbone of the anhydride (monomer and/or polymer), the amine, and/or or the hydroxy polymers.

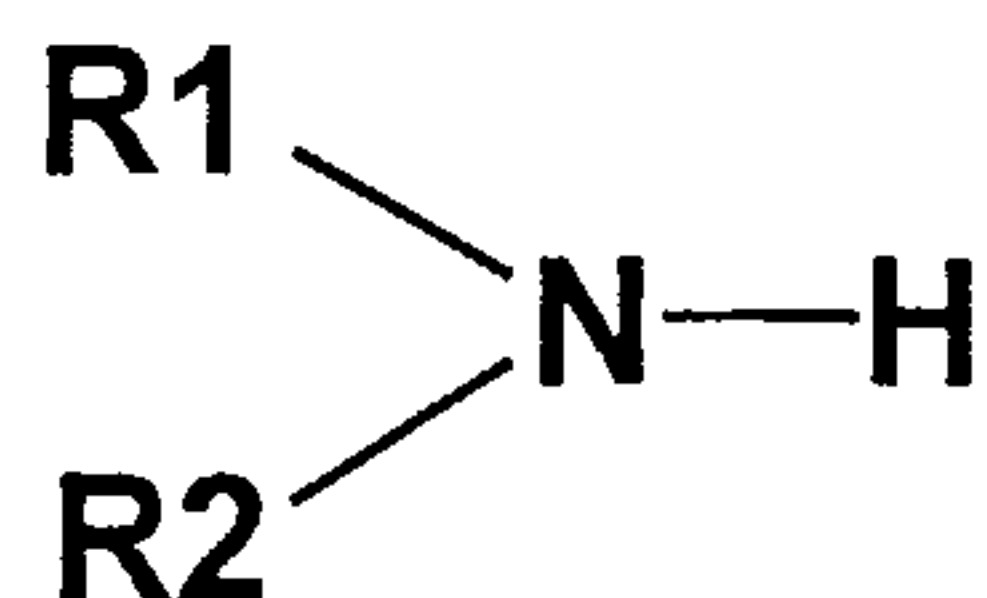
The hydroxy-functional compound can include, by way of non-limiting example, polyurethane polyols which are the reaction products of alcohols and isocyanate and are described in US Patent Nos. 5,130,405 and 5,175,227. Other hydroxy-functional compounds include polyester polyols, which are derived from the condensation of polycarboxylic acids and/or anhydrides and polyols. Specific examples of polycarboxylic acids include maleic, succinic, phthalic, adipic, trimellitic, cyclohexanedicarboxylic acids and/or anhydrides. Selected examples of polyols

which can react with the carboxylic acids and/or the anhydride to form the polyester polyols include ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, dipropylene glycol, 1-3, propane diol, 1-4 butanediol, 1-5 pentanediol, 1,6-hexanediol, 1-4 cyclohexanedimethanol, neopentyl glycol, 2,2,4-trimethyl 1,3 pentanediol, 2,2-butyl, ethyl 1-3 propanediol, 2,2 bis(4-hydroxycyclohexyl)propane, bis(4-hydroxycyclohexyl)methane, trimethylolethane, trimethylolpropane, glycerol, pentaerythritol, dipentaerythritol, sorbitol, etc.

Monoalcohol and/or monoacids may be used in the preparation of these polyesterpolyols as a modifier or co-reactant. The reaction between

acids/anhydride and polyols is usually conducted under condensation polymerization conditions where water is removed azeotropically to the desired molecular weight, hydroxy and acid values. Certain polyols can be modified with carprolactone to impart molecular weight extension, flexibility, and reactivity.

Other hydroxy-functional compounds include polyether polyols, which are known in the art and can be prepared, for example, by reacting a diol, a triol or a polyol with alkylene oxide. Representative examples include polyethylene glycol and polypropylene glycols. Another class of hydroxy-functional compounds includes the reaction products of monomeric and or polymeric amines and epoxides. The amines are secondary ones having the following general structure:



where R1 & R2 =

- 1) C1 to C18 alkyl/aryl radical- linear or branched, cyclic and/or acyclic, aliphatic and/or aromatic, saturated and/or unsaturated
- 2) C1 to C18 hydroxyalkyl/aryl radical having linear or branched, cyclic and/or acyclic, aliphatic and/or aromatic, saturated and/or unsaturated
- 3) Combination of 1) & 2)
- 4) 1) and/or 2) having non-reactive substituents such as CN, OR, OOCR, Cl, F, Br, I, NO₂, amide, carbamate etc.,

Representative examples of the amine include diethanol amine, N-methylethanol amine, dimethyl amine, dibutyl amine, benzylmethyl amine, substituted and unsubstituted piperidine and piperazine, etc. Representative examples of the

5 epoxides used as a co-reactant with the secondary amines include ethylene oxide, propylene oxide, acrylic co-polymers of glycidyl acrylate and/or methacrylate with styrene and acrylic or methacrylic monomers, and the reaction products of epichlorohydrine with polyhydric alcohol or phenol such as those known as bisphenol-A or F based epoxides. These commercially available epoxides are

10 known as Epon™, DER™ or Araldite™ from Resolution Performance Products, Dow Chemical Co. or Ciba-Geigy Corp. respectively. Other epoxides useful as co-reactants with the secondary amines to produce the hydroxy-functional compounds are those described in the following section, which details the teaching of the epoxides useful in this invention.

15

Other useful hydroxy-functional compounds include acrylic and styrene copolymers with hydroxy-functional monomers. These hydroxy-functional compounds are conveniently prepared by copolymerizing under a free-radical

polymerization condition a mixture of ethylenically unsaturated monomers comprising a) 5-70 mole % hydroxy-functional monomers, b) 0-50 mole% styrene, c) 5-95 mole % alkyl acrylate and/or methacrylate, and d) 0-50 mole % carboxyl, epoxy and/or tertiary amine-functional compounds. Examples of hydroxy-functional monomers include hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, 4-hydroxybutyl acrylate, 4-hydroxy butyl methacrylate, various caprolactone-modified hydroxy-functional monomers available from Dow Chemicals under the trade name Tone Monomers™ or from Daicel Chemical Industries under the trade name Placel™, reaction product of acrylic acid or methacrylic acid with Cardura™ E-10 from Shell Chemicals and the like. Examples of the alkyl acrylate or methacrylate include non-functional acrylate and methacrylate having 1-18 carbons where the alkyl group is a linear or branched alkyl radical such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, dodecyl, 2-ethylhexyl, cyclohexyl, etc.

Other representative examples of hydroxy-functional compounds include the reaction products of epoxy-functional polymers and saturated fatty carboxylic acid such as isonanoic acid, the reaction products of acid-functional polymers with epoxy-functional compounds such as Cardura E-10™ from Shell Chemicals.

Non-limiting examples of epoxy-functional compounds include aromatic and aliphatic epoxides. The preferred epoxy-functional compounds are aliphatic and cycloaliphatic epoxy for durability purposes. These include compounds having two or more epoxy groups such as those based on glycidyl ethers, esters, acrylic polymers, urethane (such as, for example, urethane from isocyanates and glycidyl alcohol), epoxidized oils; cycloaliphatic epoxides or a mixture thereof. Specific non-limiting examples include acrylic polymers obtained by the free-radical polymerization of glycidyl acrylate or methacrylate monomers with other free-radically copolymerizable monomers, such as styrene, alkyl (meth)acrylate,

hydroxyethyl (meth) acrylate, and any other co-polymerizable monomers. Non-limiting examples also include polyglycidyl ether of polyols such as trimethylol ethane or propane, pentaerythritol, neopentyl glycol, and the like (having 2 or more epoxy groups), 3,4-epoxy cyclohexylmethyl, and/or 3, 4-epoxycyclohexane carboxylate. Additional non-limiting examples include tri 3,4-epoxycyclohexane carboxylate esters of trimethylol ethane or propane or tetra 3,4-epoxycyclohexane carboxylate ester of pentaerythritol ; also see examples described in US Patent No. 6,201,070; sorbitol polyglycidyl ether known as DENACOLTM from Nagase America Corporation, and mixtures thereof. Preferably, the epoxy-functional compound is a cycloaliphatic epoxide and/or an acrylic copolymer made by the free-radical polymerization of styrene, alkyl acrylate and methacrylate with hydroxyethyl methacrylate and/or acrylate and glycidyl methacrylate and/or acrylate.

The preferred anhydrides are monoanhydride and/or anhydride-functional polymers based on polymerizing an ethylenically unsaturated monoanhydride monomer with one or more other ethylenically unsaturated monomer (s) copolymerizable with the ethylenically unsaturated monoanhydride monomer. Non-limiting examples of ethylenically unsaturated monoanhydride monomer include : itaconic anhydride, maleic anhydride, alkenyl succinic anhydride such as allyl succinic anhydride, ethyl-butenylsuccinic anhydride and the like. Non-limiting examples of copolymerizable ethylenically unsaturated monomers include styrene, alkyl (meth) acrylate where the alkyl group contains from 1-18 carbon atoms, and/or alpha olefin monomers including 1-alkenes such as 1-pentene, 1-hexene, 1-heptene, 1-octene, etc.

Representative examples of monoanhydrides in the composition include phthalic anhydride, tetra- and hexahydrophthalic anhydride, 4-methylhexahydrophthalic anhydride, 3,6-endomethylene-4-tetrahydrophthalic

anhydride, methyl-3,6-endomethylene-tetrahydrophthalic anhydride (methylnadic anhydride), 3,4,5,6,7,7-hexachloro-3,6-endomethylene-tetrahydrophthalic anhydride, succinic anhydride, butenylsuccinic anhydride, dodecenyl-succinic anhydride; pyromellitic dianhydride, or mixtures of such anhydrides.

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The anhydride-functional polymer can alternatively be an ene-adduct of an unsaturated anhydride such as maleic anhydride to a diene polymer such as unsaturated oil, drying alkyds, polyester or unsaturated polymers such as butadiene polymers and copolymers and the metathesis polymers of cyclooctene.

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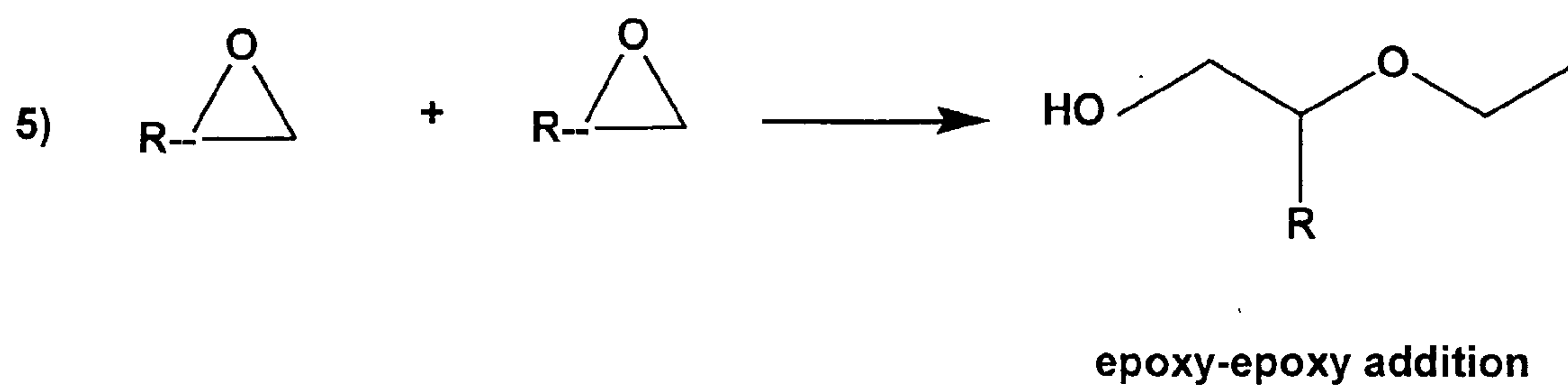
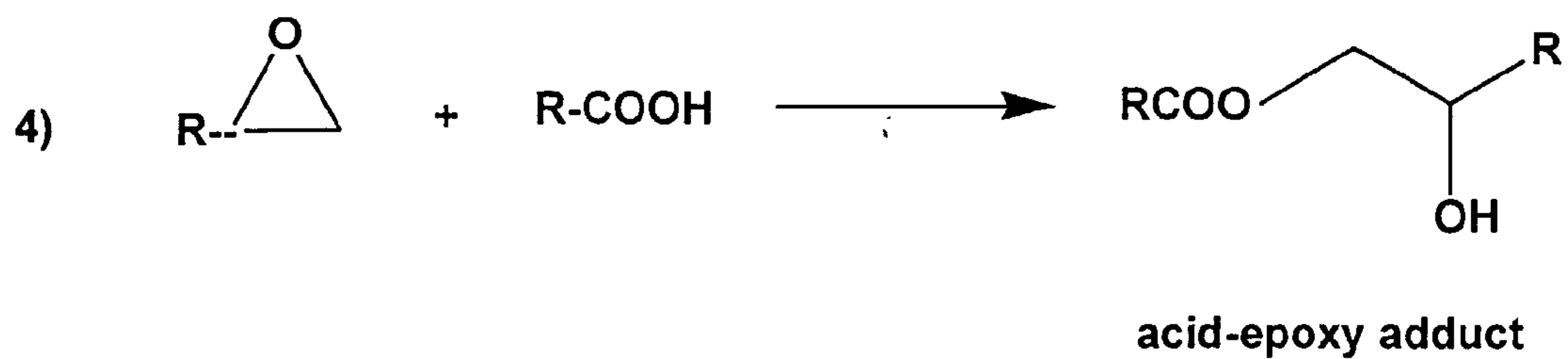
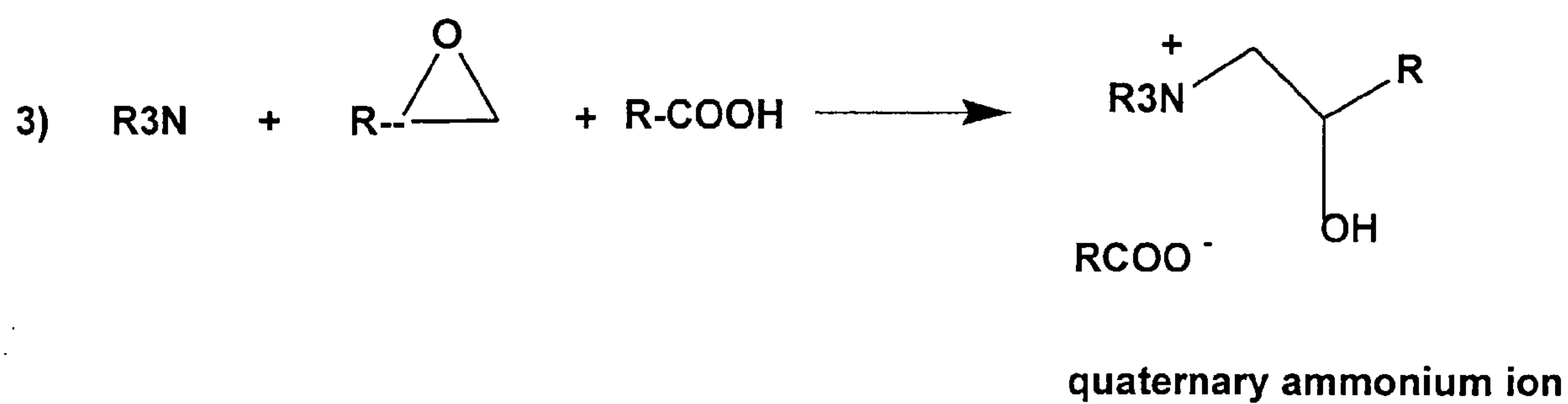
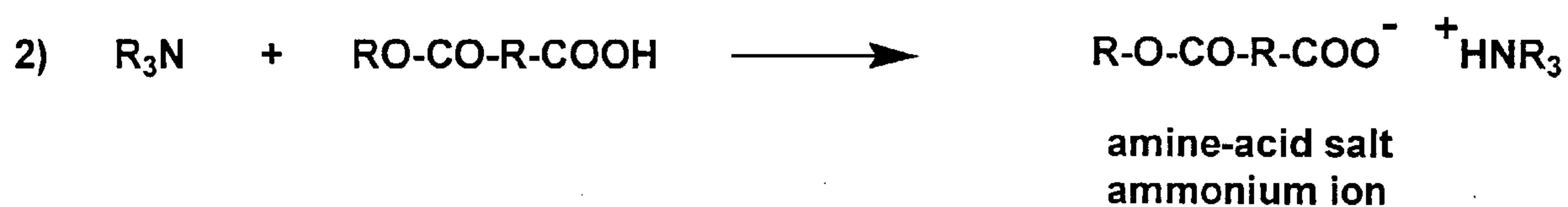
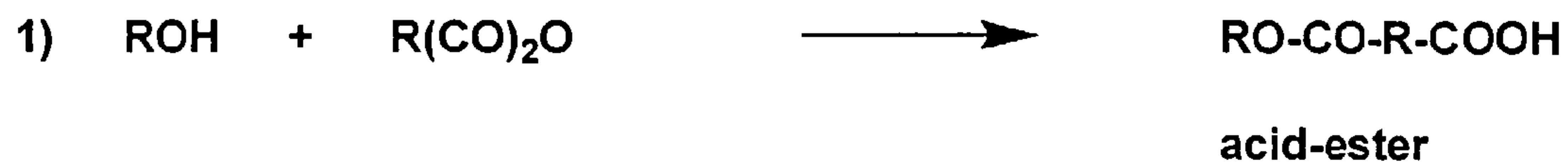
The presence of the acid/carboxyl-functional compound is optional. This acid can be a mono-functional compound, such as acetic acid, and/or higher molecular weight acids and fatty acids or a poly-functional compound. Polymeric acids include, by way of non-limiting example, (meth) acrylate, polyesters, polyester urethanes and the like. Representative examples of the polymeric acrylic acids include copolymers of ethylenically unsaturated organic acids with ethylenically unsaturated monomers copolymerizable with the ethylenically unsaturated organic acids. Representative examples of ethylenically unsaturated organic acids include acrylic acid, methacrylic acid, crotonic acid, tiglic acid, 3,3-dimethylacrylic acid, trans-2-pentenoic acid, 4-pentenoic acid, trans-2-methyl-2-pentenoic acid, 6-heptenoic acid, 2-octenoic acid, and the like. Preferred unsaturated organic acids include acrylic acid, methacrylic acid, and mixtures thereof where the average acid equivalent weight is, for example, at least 46. Representative examples of the mono-functional acid include acetic acid, propanoic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, isonanoic acid, dodecanoic acid, palmitic acid, stearic acid, isostearic acid, mixtures thereof and the like.

25

The coating composition can be applied in any known manner, for example by brushing, spraying, dipping, roll coatings, flow coatings or any other method employed for applying coatings. It is then dried at ambient or bake conditions. Possible chemical reactions that can take place during the cure time are shown

5 below:

17



Reaction 1 is the fastest reaction leading to a permanent cross-linking if the anhydride and hydroxy are in polymeric forms. It is catalyzed by the presence of the tertiary amine polymer which also substantially contributes to the three dimensional network. If only the anhydride-functional compound is monomeric, then the hydroxyl groups are converted to acid groups, which will react further with the epoxy and amine. Reaction 1 also provides the desirable early hardness development. Reaction 2 proceeds immediately after the completion of Reaction 1. Reaction 3 proceeds at a slower rate than Reaction 1 and provides additional cross-links, thus enhancing the overall cure of the system. However, its contribution to the network is substantial at higher levels of the amines. It is more pronounced when the epoxy compound is a glycidyl type. When the epoxy compound is an aliphatic or cycloaliphatic epoxy, Reaction 4 is the dominant reaction and requires higher reaction temperatures. Several other reactions are possible.

15

The coatings of the present invention may typically be applied to any substrate such as metal, plastic, glass, wood, synthetic fibers, various synthetic composites, etc. by brushing, spraying, dipping, roll coatings, flow coatings or any other method employed for applying coatings. The applied coatings are allowed to cure at ambient temperatures or baked at anywhere from about 120°F (49°C) to about 400°F (204°C), such as from about 150°F (66°C) to about 200°F (93°C), for about 20-40 minutes or 250°F (121°C) to 350°F (177°C) for about 15-20 minutes. The time and temperature depend upon the type of substrate, its thermal stability, the method of heat or energy transfer and the efficiency of that transfer.

25

By way of example, the coating composition of the present invention has a solids content of about 20-80% by weight binder and 80-20% by weight water and/or organic solvent(s).

The coatings of the present invention may typically be used as primers, undercoats, basecoats, clearcoats, and/or topcoats. Among the preferred applications of the present invention are: 1) clearcoat/basecoat for automotive coatings formulations; 2) topcoat for general industrial metal coatings formulations; 5 3) primers, sealers, clearcoat and basecoats for wood coatings formulations; and 4) primers and topcoats for plastic coatings formulations.

The present invention has been demonstrated to give superior coatings properties compared to the previously known systems. This is shown by the 10 following examples, which represent several embodiments of the composition, preparation, and performance advantages of the present invention, and are not intended to limit the scope of the invention. All parts are by weight unless otherwise specified.

15 Examples 1-17 are examples of the preparation of polymers useful in the composition of the present invention.

Example 1:

20 Preparation of Anhydride-Functional Acrylic Polymer

To a five liter, four neck reaction flask equipped with a Dean-Stark trap, condenser, agitator, heating mantle, FMI liquid metering pumps and thermocouple attached to an L11-1500 Thermowatch, 1440.18 parts of aromatic 100 was charged and 25 heated to a reflux temperature of 325°F (163°C). A pre-mixture of 802.4 parts of butyl methacrylate, 802.4 parts of styrene, 802.4 parts of butyl acrylate, 267.5 parts of maleic anhydride and 40.12 parts of tert-butyl peroxybenzoate were added over 3 hours via an FMI QG50 monomer pump. The temperature was held at the reflux point of aromatic 100 throughout the monomer addition. The reaction mixture was

then held for 1 hour to allow for completion of the polymerization reaction. A small amount of chaser initiator, 2.16 parts of tert-butyl peroxybenzoate, was then added and the reaction mixture was held for an additional hour at reflux. The reaction mixture was then cooled and thinned with a mixture of 51.29 parts of aromatic 100 and 291.61 parts of methyl amyl ketone (MAK). The thinned resin solution was then discharged and filtered. The Gardner Holdt viscosity at the corresponding % solids of the resultant resin was N-O at 60.3% solids and A1-A at 50% solids in MAK. The weight average molecular weight was 4450.

10 Example 2:

Preparation of Anhydride-Functional Acrylic Polymer

A five-liter reaction vessel equipped similarly to that used in Example 1 was charged with 1440.18 parts of aromatic 100 and heated to its reflux temperature of 325°F (163°C). A pre-mixture of 668.66 parts of methyl methacrylate, 668.66 parts of styrene, 668.66 parts of butyl acrylate, 668.66 parts of maleic anhydride and 40.12 parts of tert-butyl peroxybenzoate was added over 3 hours via an FMI QG50 monomer pump. The temperature was held at the reflux point of aromatic 100 throughout the monomer addition. The reaction mixture was then held 1 hour to allow for completion of the polymerization reaction. A small amount of chaser initiator, 2.16 parts of tert-butyl peroxybenzoate, was then added and the reaction mixture was held for an additional hour at reflux. The reaction mixture was then cooled and thinned with a mixture of 51.29 parts of aromatic 100 and 291.61 parts of methyl amyl ketone. The thinned resin solution was then discharged and filtered. The Gardner Holdt viscosity at the corresponding % solids of the resultant resin was: Z5-Z6 at 59.4% solids and J-K at 50% solids in MAK. The weight average molecular weight was 3900.

Example 3:

Preparation of Anhydride-Acid-functional Acrylic Polymer

- 5 A five-liter reaction vessel equipped similarly to that used in Example 1 was charged with 1440.18 parts of aromatic 100 and heated to its reflux temperature of 325°F (163°C). A pre-mixture of 588.87 parts of methyl methacrylate, 588.87 parts of styrene, 588.87 parts of butyl acrylate, 668.66 parts of maleic anhydride, 239.38 parts of acrylic acid and 40.12 parts of tert-butyl peroxybenzoate was added over 3
- 10 hours via an FMI QG50 monomer pump. The temperature was held at the reflux point of aromatic 100 throughout the monomer addition. The reaction mixture was held 1 hour after the monomer addition was complete to allow for completion of the polymerization reaction. A small amount of chaser initiator, 2.16 parts of tert-butyl peroxybenzoate, was then added and the reaction mixture was held for an
- 15 additional hour at reflux. The reaction mixture was then cooled, thinned with 342.90 parts of aromatic 100 and 405.27 parts of methyl amyl ketone and then filtered. The Gardner Holdt viscosity at the corresponding % solids of the resultant resin was: Z4-Z5 at 59.4% solids and U-V at 50% solids in MAK. The weight average molecular weight was 3600.

20

Example 4 :

Preparation of Anhydride-Functional Acrylic Polymer

- 25 A three-liter reaction vessel equipped similarly to that used in Example 1 was charged with 800.49 parts of aromatic 100 and heated to its reflux temperature of 325°F (163°C). A pre-mixture of 371.66 parts of methyl methacrylate, 371.66 parts of styrene, 371.66 parts of butyl acrylate, 371.66 parts of maleic anhydride and 22.30 parts of tert-butyl peroxybenzoate was added over 3 hours via an FMI QG50

monomer pump. The temperature was held at the reflux point of aromatic 100 throughout the monomer addition. The reaction mixture was then held 1 hour to allow for completion of the polymerization reaction. A small amount of chaser initiator, 1.20 parts of tert-butyl peroxybenzoate, was then added and the reaction
5 mixture was held for an additional hour at reflux. The reaction mixture was then cooled and thinned with a mixture of 190.59 parts of methyl amyl ketone. The thinned resin solution was then discharged and filtered. The Gardner Holdt viscosity at the corresponding % solids of the resultant resin was: Z4-Z5 at 59.7% solids and J-K at 50% solids in MAK. The weight average molecular weight was
10 5400.

Example 5:

Preparation of Anhydride-Functional Acrylic Polymer

15 A five-liter reaction vessel equipped similarly to that used in Example 1 was charged with 1440.18 parts of aromatic 100 and 401.18 parts of maleic anhydride and heated to its reflux temperature of 325°F (163°C). A pre-mixture of 802.4 parts of butyl acrylate, 802.4 parts of styrene, 668.63 parts of maleic anhydride and
20 40.12 parts of tert-butyl peroxybenzoate was added over 3 hours via an FMI QG50 monomer pump. The temperature was held at the reflux point of aromatic 100 throughout the monomer addition. The reaction mixture was then held at the reflux point of aromatic 100 for 1 hour to allow for completion of the polymerization reaction. A small amount of chaser initiator, 2.16 parts of tert-butyl
25 peroxybenzoate, was then added and the reaction mixture was held for an additional hour at reflux to complete the polymerization. A second 2.16 parts of tert-butyl peroxybenzoate was then added and held for another hour to complete the polymerization. The reaction mixture was then cooled and thinned with 342.90 parts of methyl amyl ketone. The thinned resin solution was then discharged and

filtered. The Gardner Holdt viscosity at the corresponding % solids of the resultant resin was Z3 at 60.4% solids and D-E at 50% solids in MAK. The weight average molecular weight was 2400.

5 Example 6:

Preparation of Epoxy-Functional Acrylic Polymer

A five-liter reaction vessel equipped similarly to that used in Example 1 was
10 charged with 1499.18 parts of butyl acetate and heated to 260-270°F (127-132°C).
A pre-mixture of 823.55 parts of styrene, 880.32 parts of butyl acrylate, 207.33
parts butyl methacrylate, 636.02 parts of glycidyl methacrylate and 254.84 parts of
tert-butyl peroxy-3,5,5-trimethylhexanoate was added over 3 hours through an FMI
QG50 monomer pump. The reaction mixture was held at 260-270°F (127-132°C)
15 throughout the monomer addition. The reaction mixture was then held at 260-
270°F (127-132°C) for 1 hour to allow for completion of the polymerization reaction.
The mixture was then cooled, thinned with 198.76 parts of butyl acetate and
filtered. The Gardner Holdt viscosity at the corresponding % solids of the resultant
resin was: F at 60.6% solids, and A₂-A₁ at 50% solids in n-butyl acetate. The
20 weight average molecular weight was 6300.

Example 7:

Preparation of Epoxy-Functional Acrylic Polymer

25

A five-liter reaction vessel equipped similarly to that used in Example 1 was
charged with 1499.18 parts of butyl acetate and heated to 260-270°F (127-132°C).
A pre-mixture of 636.75 parts of styrene, 636.75 parts of butyl acrylate, 509.44
parts butyl methacrylate, 764.17 parts of glycidyl methacrylate and 254.84 parts of

tert-butyl peroxy-3,5,5-trimethylhexanoate was added over 3 hours through an FMI QG50 monomer pump. The temperature was held at 260-270°F (127-132°C) throughout the monomer addition. The reaction mixture was then held at 260-270°F (127-132°C) for 1 hour to allow for completion of the polymerization reaction.

5 The mixture was then cooled, thinned with 198.76 parts of butyl acetate and filtered. The Gardner Holdt viscosity at the corresponding % solids of the resultant resin was H-I at 60.5% solids and A1-A at 50% solids in butyl acetate. The weight average molecular weight was 7050.

10 Example 8 :

Preparation of Epoxy and Hydroxy-Functional Acrylic Polymer

A three-liter reaction vessel equipped similarly to that used in Example 1 was
15 charged with 766.35 parts methyl amyl ketone and heated to 260-270°F (127-132°C). A pre-mixture of 390.6 parts styrene, 390.6 parts butyl acrylate, 130.2 parts 2-hydroxyethyl methacrylate, 390.6 parts glycidyl methacrylate and 130.27 parts tert-butyl peroxy-3,5,5-trimethylhexanoate was added over 3 hours through a monomer pump. The temperature was held at 260-270°F (127-132°C) throughout
20 the monomer addition. The reaction mixture was then held at 260-270°F (127-132°C) for 1 hour after the monomer addition to allow for completion of the polymerization reaction. At this point the mixture was cooled, thinned with 101.60 parts of methyl amyl ketone and then filtered. The Gardner Holdt viscosity at the corresponding % solids of the resultant resin was H-I at 60.5% solids and A1-A at
25 50% solids in MAK. The weight average molecular weight was 4700.

Example 9:

Preparation of Epoxy and Hydroxy-Functional Acrylic Polymer

5 A three-liter reaction vessel equipped similarly to that used in Example 1 was charged with 766.35 parts n-butyl acetate and heated to 255-265°F (124-129°C). A pre-mixture of 420.98 parts styrene, 450.00 parts butyl acrylate, 105.98 parts 2-hydroxyethyl methacrylate, 325.12 parts glycidyl methacrylate and 130.27 parts tert-butyl peroxy-3,5,5-trimethylhexanoate was added over 3 hours through a
10 monomer pump. The temperature was held at 255-265°F (124-129°C) throughout the monomer addition. The reaction mixture was then held at 255-265°F (124-129°C) for 1 hour after the monomer addition to allow for completion of the polymerization reaction. At this point the mixture was cooled, thinned with 101.60 parts of n-butyl acetate and then filtered. The Gardner Holdt viscosity of the
15 resultant resin was H-J at 60 % solids in n-butyl acetate.

Example 10:

Preparation of Epoxy and Hydroxy-Functional Acrylic Polymer

20 A three-liter reaction vessel equipped similarly to that used in Example 1 was charged with 766.35 parts methyl amyl ketone and heated to 260-270°F (127-132°C). A pre-mixture of 420.98 parts styrene, 450.00 parts butyl acrylate, 105.98 parts 2-hydroxyethyl methacrylate, 325.12 parts glycidyl methacrylate and 130.27
25 parts tert-butyl peroxy-3,5,5-trimethylhexanoate was added over 3 hours through a monomer pump. The temperature was held at 260-270°F (127-132°C) throughout the monomer addition. The reaction mixture was then held at 260-270°F (127-132°C) for 1 hour after the monomer addition to allow for completion of the polymerization reaction. At this point the mixture was cooled, thinned with 101.60

parts of methyl amyl ketone and then filtered. The Gardner Holdt viscosity of the resultant resin was: F-I at 60 % solids in MAK.

Example 11:

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Preparation of Epoxy and Hydroxy-Functional Acrylic Polymer

A three-liter reaction vessel equipped similarly to that used in Example 1 was charged with 766.35 parts methyl amyl ketone and heated to 260-270°F (127-132°C). A pre-mixture of 455.7 parts styrene, 520.8 parts butyl acrylate, 130.2 parts 2-hydroxyethyl acrylate, 195.3 parts glycidyl methacrylate and 130.27 parts tert-butyl peroxy-3,5,5-trimethylhexanoate was added over 3 hours through a monomer pump. The temperature was held at 260-270°F (127-132°C) throughout the monomer addition. The reaction mixture was then held at 260-270°F (127-132°C) for 1 hour after the monomer addition to allow for completion of the polymerization reaction. At this point, the mixture was cooled, thinned with 101.60 parts of methyl amyl ketone and then filtered. The Gardner Holdt viscosity at the corresponding % solids of the resultant resin was E-F at 60.5% solids and A1 at 50% solids in MAK. The weight average molecular weight was 7000.

20

Example 12:

Preparation of Tertiary-Amine and Acid-functional Acrylic Polymer

25 A five-liter reaction vessel equipped similarly to that used in Example 1 was charged with 1087.66 parts of methyl amyl ketone and heated to 212°F (100°C). A pre-mixture of 464.80 parts of methyl methacrylate, 464.8 parts of styrene, 855.93 parts of butyl acrylate, 611.14 parts of N,N-dimethylaminoethyl methacrylate, 49.06 parts of methacrylic acid, 486.90 parts of methyl amyl ketone and 129.6 parts of

2,2'-azobis(2-methylbutyronitrile) was added over 3 hours by an FMI QG50 monomer pump. The temperature was held at 212-222°F (100-106°C) throughout the monomer addition. The reaction mixture was then held at 212-222°F (100-106°C) for 1 hour to allow for completion of the polymerization reaction. A small amount of chaser initiator, 24.28 parts of 2,2'-azobis(2-methylbutyronitrile), was then added and the reaction held for an additional hour at 212-222°F (100-106°C). The reaction mixture was then thinned with 426.50 parts of methyl amyl ketone and filtered. The Gardner Holdt viscosity of the resultant resin was F-I at 55 % solids in MAK.

Example 13:

Preparation of Tertiary-Amine and Acid-functional Acrylic Polymer

A five-liter reaction vessel equipped similarly to that used in Example 1 was charged with 1087.50 parts of methyl amyl ketone and heated to 212°F (100°C). A pre-mixture of 741.56 parts of methyl methacrylate, 741.56 parts of styrene, 314.43 parts of butyl acrylate, 587.30 parts of N,N-dimethylaminoethyl methacrylate, 61.27 parts of methacrylic acid, 487.07 parts of methyl amyl ketone and 129.54 parts of 2,2'-azobis(2-methylbutyronitrile) was added over 3 hours via an FMI QG50 monomer pump. The temperature was held at 212-222°F (100-106°C) throughout the monomer addition. The reaction mixture was then held at 212-222°F (100-106°C) for 1 hour following the monomer addition to allow for completion of the polymerization reaction. A small amount of chaser initiator, 23.63 parts of 2,2'-azobis(2-methylbutyronitrile) was then added and the reaction mixture held for an additional hour at 212-222°F (100-106°C). The reaction mixture was then thinned with 426.81 parts of methyl amyl ketone and filtered. The Gardner Holdt viscosity at the corresponding % solids of the resultant resin was: S-U at 55 % solids in MAK.

Example 14:

Preparation of Tertiary-Amine, Carboxy, and Hydroxy- Functional Acrylic Polymer

5 A five-liter reaction vessel equipped similarly to that used in Example 1 was charged with 1087.50 parts of methyl amyl ketone and heated to 212°F (100°C). A pre-mixture of 608.69 parts of methyl methacrylate, 733.84 parts of styrene, 314.43 parts of butyl acrylate, 587.30 parts of N,N-dimethylaminoethyl methacrylate, 51.15 parts of acrylic acid, 150.71 parts of 2-hydroxyethyl methacrylate, 487.07 parts of
10 methyl amyl ketone and 129.54 parts of 2,2'-azobis(2-methylbutyronitrile) was added over 3 hours via an FMI QG50 monomer pump. The temperature was held at 212-222°F (100-106°C) throughout the monomer addition. The reaction mixture was then held at 212-222°F (100-106°C) for 1 hour after the monomer addition to allow for completion of the polymerization reaction. A small amount of chaser
15 initiator, 23.63 parts of 2,2'-azobis(2-methylbutyronitrile) was then added and the reaction mixture was held for an additional hour at 212-222°F (100-106°C). The mixture was then thinned with 427.00 parts of methyl amyl ketone and filtered. The Gardner Holdt viscosity at the corresponding % solids of the resultant resin was: Q-R at 54.3 % solids, and H at 50% solids in MAK. The weight average molecular
20 weight was 4800.

Example 15:

Preparation of Tertiary-Amine-functional Polymer

25

A five-liter reaction vessel equipped similarly to that used in Example 1 was charged with 1063.70 parts of methyl amyl ketone and heated to 212°F (100°C). A pre-mixture of 785.26 parts of methyl methacrylate, 725.33 parts of styrene, 307.55 parts of butyl acrylate, 574.45 parts of N,N-dimethylaminoethyl methacrylate,

476.41 parts of methyl amyl ketone and 126.71 parts of 2,2'-azobis(2-methylbutyronitrile) was added over 3 hours via an FMI QG50 monomer pump. The temperature was held at 212-222°F (100-106°C) throughout the monomer addition. The reaction mixture was then held at 212-222°F (100-106°C) for an additional hour to allow for completion of the polymerization reaction. A small amount of chaser initiator, 23.11 parts of 2,2'-azobis(2-methylbutyronitrile), was then added and the reaction mixture was held for an additional hour at 212-222°F (100-106°C). The mixture was then thinned with 417.48 parts of methyl amyl ketone and filtered. The Gardner Holdt viscosity at the corresponding % solids of the resultant resin was: T-U at 59.8 % solids, and C-D at 50% solids in MAK. The weight average molecular weight was 6000.

Example 16:

15 Preparation of Tertiary-Amine and Hydroxy- Functional Polymer

A five-liter reaction vessel equipped similarly to that used in Example 1 was charged with 945.51 parts of methyl amyl ketone and heated to 212°F. A pre-mixture of 573.69 parts of methyl methacrylate, 638.03 parts of styrene, 273.38 parts of butyl acrylate, 510.62 parts of N,N-dimethylaminoethyl methacrylate, 131.03 parts of 2-hydroxyethyl methacrylate, 423.48 parts of methyl amyl ketone and 112.62 parts of 2,2'-azobis(2-methylbutyronitrile) was added over 3 hours via an FMI QG50 monomer pump. The temperature was held at 212-222°F (100-106°C) throughout the monomer addition. The reaction mixture was then held at 212-222°F (100-106°C) for an additional hour to allow for completion of the polymerization reaction. A small amount of chaser initiator, 20.54 parts of 2,2'-azobis(2-methylbutyronitrile) was then added and the reaction mixture was held for an additional hour at 212-222°F (100-106°C). The mixture was then thinned with 371.09 parts of methyl amyl ketone and filtered. The Gardner Holdt viscosity at the

corresponding % solids of the resultant resin was: J-K at 55.5 % solids, and D at 50% solids in MAK. The weight average molecular weight was 5500.

Example 17:

5

Preparation of Acid-functional Polymer

A five-liter reaction vessel equipped similarly to that used in Example 1, with a recycling receiver replacing the Dean-Stark trap was charged with 1164.34 parts of ethyl 3-ethoxypropionate and heated to its reflux temperature of 325°F (163°C). A
10 pre-mixture of 707.72 parts of styrene, 1783.17 parts of butyl acrylate, 339.99 parts acrylic acid and 246.16 parts of tert-butyl peroxybenzoate was added over 3 hours via an FMI QG50 monomer pump. The temperature was held at the reflux point of ethyl 3-ethoxypropionate throughout the monomer addition; it was necessary to
15 occasionally remove volatile by-products of the initiator decomposition through the recycling receiver in order to maintain a 320°F (160°C) minimum polymerization temperature. The reaction mixture was then held at reflux for an additional hour to allow for completion of the polymerization reaction. The ethyl 3-ethoxypropionate was then removed under vacuum and the resulting resin thinned with 707.72 parts
20 of butyl acetate. The thinned resin solution was then discharged from the reactor and filtered through a 25-micron bag. The Gardner Holdt viscosity at the corresponding % solids of the resultant resin was: Z4 at 80.5 % solids, and D-E at 60% solids in n-butyl acetate. The weight average molecular weight was 3800.

25 Example 18:

Comparative Example for a Clear Coat System

This is a comparative example where a mixture of tertiary amine-, acid-, hydroxy-
30 and epoxy-functional compounds are used.

Component A

Resin A (a hydroxy- and epoxy-functional resin of Example 9)	544.33
--	--------

5 Component B

Resin B (a tertiary-amine and acid-functional resin of Example 13)	<u>455.67</u>
--	---------------

Total	1000.00
-------	---------

- 10 The two Components, A and B, can be mixed together in the weight ratios indicated and applied as a thin clear film. The coatings performance of this example is compared against the coatings performance of the present invention as illustrated in Examples 19-20.

Examples 19 and 20:

15 Clearcoat Examples

The following two clearcoats were prepared according to the following mixing ratios:

20 Example 19:

Component A

Resin A (a hydroxy- and epoxy-functional resin of Example 9)	517.87
--	--------

25 Component B

Resin B (a tertiary-amine and acid-functional resin of Example 13)	433.60
--	--------

32

Component C

Resin C (an anhydride-functional resin of Example 4) 48.53

Total 1000.00

5 Example 20:

Component A

Resin A (a hydroxy- and epoxy-functional resin of Example 9) 482.73

10 Component B

Resin B (a tertiary-amine- and acid-functional resin of Example 13) 404.13

Component C

15

Resin C (an anhydride-functional resin of Example 4) 113.13

Total 1000.00

20 When ready to use, Components A, B and C are mixed together in the weight ratios indicated.

25 Films of the Comparative Example (Example 18) and Examples 19 and 20 were prepared by using a three mil (wet film thickness) applicator bar on a glass plate and then baking for 20 minutes at 180°F (82°C). Film properties were measured 24 hours after application without baking. Such physical properties as hardness, solvent resistance (MEK) and fingerprint resistance were measured. The film properties are compared in Table 1.

Table 1. Clear Coatings Properties of Baked and Ambient Cure Enamels.

Properties after baking 20 minutes at 180°F (82°C)			
	Example 18 Comparative Example	Example 19	Example 20
Fingerprinting out of oven	Prints	No printing	No Printing
König hardness	107	120	134
50 double MEK rubs, relative effect*	3	5	7
Double MEK rubs to break film to substrate	50	100	200
Properties after Air Drying (24 hours)			
König Pendulum hardness	47	51	64
Dry Times (ASTM D1640):			
Set to Touch	<5 minutes	<5 minutes	<5 minutes
Dust free	10 minutes	10 minutes	10 minutes
Dry hard	8 hours	6 hours	2 ½ hours

* 10= no effect, 0=complete dissolving

- 5 The data of Table 1 clearly indicate the superiority of the present invention (Examples 19 and 20) over the comparative example (Example 18) where drying, hardness and solvent resistance were superior for both ambient or baked clearcoat applications.

10 Example 21:

Comparative Example for a 2K White Pigmented Enamel

- This is a comparative example where a mixture of tertiary amine-, acid-, hydroxy- and epoxy-functional compounds are used in a pigmented single stage enamel formulation.
- 15

Several commercially available products are used in this example:

Product	Source	Function	Description
Byk Anti-terra 203™	BYK-Chemie	Pigment wetting agent	Alkylammonium salt of a polycarboxylic acid
Byk 066™	BYK-Chemie	Defoamer	Polysiloxane
Kronos 2310™	Kronos	Hiding pigment	Titanium Dioxide
Blanc fixe micro	Sachleben	Inert filler pigment	Barium Sulfate
Byk 331™	BYK-Chemie	Surfactant	Polyether modified polydimethylsiloxane
Byk 358™	BYK-Chemie	Surfactant	Acrylic copolymer
Tinuvin 123™	Ciba	Light stabilizer	Hindered amine CAS No.129757-67-1

Component A:

5

Resin A (a hydroxy- and epoxy-functional resin of Example 9) 264.04

Byk Antitertra 203™ 0.51

Byk 066™ 0.80

Kronos 2310™ 268.42

10 Blanc fixe micro 151.47

The above mixture was dispersed in a High Speed Disperser to 6.5-7.0 Hegman Gauge fineness to which was added:

Byk 331™ 0.85

15 Byk 358™ 1.13

Tinuvin 123™ 2.76

Component B:

Resin B (a tertiary-amine and acid-functional resin of Example 13) 217.39

20 Methyl amyl ketone 92.63

Total 1000.00

The two Components, A and B, can be mixed together in the weight ratios indicated and applied as a pigmented white film. The coatings performance of this example was compared against the coatings performance of the present invention as illustrated in Examples 22-23.

5 Examples 22 and 23:

Pigmented Single Stage Enamels

The same commercial products described in example 21 are used in the following white single stage enamels. These examples were prepared according to the
10 present invention using the following mixing ratios:

Example 22:

Component A

15	Resin A (a hydroxy- and epoxy-functional resin of Example 9)	190.88
	Byk Antitertra 203™	0.51
	Byk 066™	0.77
	Kronos 2310™	267.85
	Blanc fixe micro	151.15
20	The above mixture was dispersed in a High Speed Disperser to 6.5-7.0 Hegman Gauge fineness to which was added:	
	Byk 331™	0.82
	Byk 358™	1.08
	Tinuvin 123™	2.68
25	Methyl amyl ketone	9.14

Component B

Resin B (a tertiary-amine and acid-functional resin of Example 13) 248.72

Methyl amyl ketone 5.60

5

Component C

Resin C (an anhydride-functional resin of Example 4) 40.80

Total 1000.00

- 10 When ready to use, Components A, B and C are mixed together in the weight ratios indicated.

Example 23:

Component A

15

Resin A (a hydroxy- and epoxy-functional resin of Example 9) 184.05

Byk Antitertra 203™ 0.51

Byk 066™ 0.78

Kronos 2310™ 267.94

20 Blanc fixe micro 151.21

The above mixture was dispersed in a High Speed Disperser to 6.5-7.0 Hegman Gage fineness to which was added:

Byk 331™ 0.79

25 Byk 358™ 1.05

Tinuvin 123™ 2.59

Methyl amyl ketone 28.10

Component B

Resin B (a tertiary-amine and acid-functional resin of Example 13) 239.82

Methyl amyl ketone 66.96

5

Component C

Resin C (an anhydride-functional resin of Example 4) 56.20

Total 1000.00

10

When ready to use, Components A, B and C can be mixed together in the weight ratios indicated above to give white single stage coatings with a volatile organic content (VOC) of 3.5 lbs./gal. and % solids of 70%.

15 A three-mil applicator bar was used to apply films to a glass plate. Selected early coatings properties were measured and compared against Comparative Example 21 as the control.

Table 2. Film properties of pigmented (white) enamels.

20

	Example 21 Comparative Example	Example 22	Example 23
% Solids	70	70	70
VOC, (lbs./gal)	3.5	3.5	3.5
Dry Times (ASTM D1640):			
Set to Touch	6 minutes	6 minutes	5 minutes
Dust free	9 minutes	8 minutes	7 minutes
Dry hard	8 hours	3 ½ hours	2 hours
Dry Through	9 hours	4 hours	3 hours
Properties after 24 hours:			
König Pendulum Hardness	35	42	53

The data of Table 2 clearly illustrate the superiority of the present invention (Examples 22 and 23) over Comparative Example 21 where drying and hardness are superior for pigmented single stage applications.

Examples 24 - 29:

5 Clearcoat Enamel Formulations Utilizing Blends of Monomeric and Polymeric Anhydride

Examples 24-28 have the following identical % mole ratio of functionalities:

10 Epoxy/Amine/Hydroxyl/ Carboxyl/Anhydride: 45/32/10/0/13 mole% (or 1.4/1.0/0.31/0/0.41 mole ratio). However, the anhydride type has been changed from 100% monomeric to 100% polymeric and mixtures of the two resins. Example 29 is a comparative example without anhydride.

15 The clear coatings systems of Example 24-29 were applied over cold roll steel test panels as thin films using No. 40 Myer bar applicator. Panels were baked for 20 minutes at 180°F (82°C) and evaluated for film properties. Air dried panels were evaluated after 24 hours drying. The performance of various compositions of anhydride (monomeric/polymeric) compared to existing technology can be seen in

Table 3.

Examples: 24-29

Example No. Coatings Component/	Example 24	Example 25	Example 26	Example 27	Example 28	Comparat Example
Mole % of Polymeric Anhydride (Example 2)	100%	75%	50%	25%	0%	None
Mole % of Monomeric Anhydride (see footnote) **	0%	25%	50%	75%	100%	None
Weight of Epoxy/Hydroxyl Resin from (Example 9)	469.59	473.47	477.34	481.22	485.09	501.42
Tertiary-Amine Resin from (Example 15)	357.50	360.41	363.33	366.25	369.16	None
Tertiary-Amine Resin from (Example 13)	None	None	None	None	None	452.98
Weight of Polymeric Anhydride Resin (Example 2)	91.68	68.76	45.84	22.92	None	None
Weight of Monomeric Anhydride (see footnote) **	None	9.54	19.09	28.63	38.17	None
Xylene	81.23	101.00	87.82	94.40	107.58	45.59
Total	1000	1000	1000	1000	1000	1000

** Dodecenyl succinic anhydride available form from Lubrizol: It is believed to be synthesized by the ene-reaction of maleic anhydride and dodecene.

Table 3. Performance of formulations containing monomeric and polymeric anhydride compounds

Example Number/ Property	Example 24	Example 25	Example 26	Example 27	Example 28	Comparative Example 29
Viscosity of sample, cps	325	269	233	194	167	306
	Panels baked 20 minutes at 180°F (82°C)					
König hardness	139	142	142	145	151	118
MEK, resistance (5=severe effect, 0= no effect)	2	3	4	4-5	5	5
	Panels air dried for 24 hours					
König hardness	75	74	82	81	86	66
MEK, resistance (5=severe effect, 0= no effect)	5	5	5	3	2	5

The data of Table 3 clearly illustrate the superiority of the present invention
 5 (Examples 24-28) over Comparative Example 29 where VOC or viscosities are
 lower, hardness and solvent resistance are improved over the present art.

Examples 30-31:

Clearcoat enamel formulations

10 These examples compare comparative Example 30 where a mixture of epoxy-,
 hydroxy-, and anhydride-functional polymers are catalyzed by catalytic amount of a
 tertiary-amine catalyst (benzyl dimethylamine- 0.5% on total solids) to the present

invention (Example 31) utilizing a tertiary-amine-functional polymer as a co-reactant.

Several commercially available products are used in this example:

5

Product	Source	Functionality	Comments
Setalux 27-1435™	Akzo Nobel Resins	Epoxy	Similar to Example 9
ERL-4221™	Dow Chemical	Epoxy	3,4-Epoxycyclohexyl-methyl 3,4-Epoxy-cyclohexane-carboxylate
Setal 26-1688™	Akzo Nobel Resins	Hydroxyl	Polyester polyol

The following clearcoat formulations were prepared:

	Example 30 Comparative Weight(g) Mole%		Example 31 Present Invention Weight(g) Mole%	
Component A:				
Setalux 27-1435™	106.7	25.0%	80.0	21.4%
ERL-4221™	20.6	25.0%	15.4	21.4%
Setal 26-1688™	74.1	25.0%	55.5	21.4%
Xylene	73.0		48.9	
Component B:				
Resin B (tertiary amine- functional polymer, Example 15)	None		87.7	14.3%
Catalyst: Benzyl dimethylamine	1.1 (0.5% on solids)		None	
Component C:				
Resin C (anhydride- functional polymer, Example 2)	99.0	25.0%	74.2	21.4%
Total:	374.5	100%	361.7	100%

10 When ready to use, Components A, B and C can be mixed together in the weight ratios indicated.

Test panels were prepared by drawing down the formulations with a No.45 Myer bar applicator on 16 gauge steel panels. This results in a dry film thickness of about 1.0-1.2 mils. MEK double-rubs and König Pendulum Hardness were determined.

- 5 The superiority of the present invention (Example 31) over comparative Example 30 is demonstrated by improvements in MEK resistance and better hardness values shown in Table 4.

10 Table 4. Properties of Examples 30-31.

	Example 30 Comparative	Example 31 Present Invention
MEK double-rubs after:		
20 min at 180°F (82°C)	3	7
20 min at 300°F (149°C)	31	70
König Pendulum Hardness after:		
20 min at 180°F (82°C)	3 (tacky)	50
20 min at 300°F (149°C)	62	146

Example 32

- 15 Preparation of tertiary-amine- and carboxyl-functional acrylic polymer

A five-liter reaction vessel equipped similarly to that used in Example 1 was charged with 1063.70 parts of methyl amyl ketone and heated to 212°F (100°C). A pre-mixture of 773.30 parts of methyl methacrylate, 725.33 parts of styrene, 307.55 parts of butyl acrylate, 574.45 parts of N,N-dimethylaminoethyl methacrylate, 11.96 parts of methacrylic acid, 476.41 parts of methyl amyl ketone and 126.71 parts of 2,2'-azobis(2-methylbutyronitrile) was added over 3 hours via an FMI QG50 monomer pump. The temperature was held at 212-222°F (100-106°C) throughout

the monomer addition. The reaction mixture was then held at 212-222°F (100-106°C) for 1 hour after the monomer addition to allow for completion of the polymerization reaction. A small amount of chaser initiator, 23.11 parts of 2,2'-azobis(2-methylbutyronitrile) was then added and the reaction mixture was held for
5 an additional hour at 212-222°F (100-106°C). The mixture was then thinned with 417.48 parts of methyl amyl ketone and filtered. The Gardner Holdt viscosity at the corresponding % solids of the resultant resin was L at 55.5 % solids and A1-A at 45% solids in MAK. The weight average molecular weight was 4614.

10 Example 33.

Preparation of anhydride-functional, water-dispersible acrylic polymer

A three-liter reaction vessel equipped similarly to that used in Example 1 was charged with 450.24 parts methyl amyl ketone and heated to its reflux temperature
15 of 306°F (152°C). A pre-mixture composed of 290.75 parts of butyl methacrylate, 290.75 parts of styrene, 290.75 parts of maleic anhydride, 581.50 parts of butyl acrylate, 115.36 parts of methoxy(polyethyleneglycol) methacrylate (average MW: 430), 280.00 parts of methyl amyl ketone and 52.42 parts of ethyl 3,3-di-(tert-amylperoxy)-butyrate was prepared. The pre-mixture was then divided into two
20 portions of 1369.02 parts and 532.52 parts, labeled Pre-mix A and Pre-mix B respectively. The composition of Pre-mix B was further modified by the addition of 21.00 parts of acrylic acid and 100.80 parts of 2-acrylamido-2-methyl propanesulfonic acid. Pre-mix A was added to the reaction vessel over 215
25 minutes and was followed by a 15-minute hold period at reflux. Following the hold period, Pre-mix B was added to the reaction vessel over 90 minutes. The temperature was held at the reflux point of methyl amyl ketone throughout both pre-mixture additions and for the 30 minutes following the Pre-mix B addition. A small amount of chaser initiator, 2.77 parts of ethyl 3,3-di-(tert-amylperoxy)-butyrate, was then added and the reaction mixture was held at reflux for an

additional hour to complete the polymerization. The reaction mixture was then cooled and thinned with 162.4 parts of methyl amyl ketone. The thinned resin solution was discharged and filtered. The resultant resin percent solids was 64.2% and the resin viscosity was 1400 centipoise as measured by a Brookfield LV
5 viscometer with spindle #3 at 30 rpm. The weight average molecular weight was 6200.

To disperse the resin in water, 60.0 parts of triethylamine and 624.0 parts of de-ionized water were charged to a 1-gallon metal container suspended beneath a
10 Premier Dispersator. The dispersator was set to 2000 rpm and 1538 parts of the resin were added to the amine/water mixture over 5 minutes. The dispersator speed was increased to 7000 rpm over the addition time as the level rose in the dispersion vessel, and that speed was held for 5 additional minutes following the resin addition to promote a stable dispersion. The resultant dispersion percent
15 solids was 45.6% and the viscosity was 2400 centipoise as measured by a Brookfield LV viscometer with spindle #3 at 30 rpm. The pH of the dispersion was 4.4 and the particle size as measured by a Brookhaven 90 Plus light-scattering instrument was 618 nm.

20 Example 34

Preparation of waterborne epoxy and hydroxy-functional acrylic polymer

A reactor was charged with the following ingredients: 323.1 g of deionized water, 8.21 g of Igepal®CO-897 (nonylphenol polyethylene oxide with 40 moles of
25 ethylene oxide, ex Rhodia) and 12.52 grams of Trigonox®AW-70 (70% aqueous solution of tert-butyl hydroperoxide, ex Akzo Nobel). The reactor was heated to 65° C. under a nitrogen blanket. At 65° C. a mixture of 8.5 g of styrene and 10.6 g of butyl acrylate was added to the reactor. Subsequently, a solution of 0.3 g of sodium formaldehyde sulfoxylate in 8.3 g of water was added to the reactor. In the

meantime a monomer pre-emulsion was prepared in a separate container using the following ingredients in grams.

Deionized water	400.6
Igepal® - CO-897	41.8
Poly(vinylpyrrolidon) (molecular weight 30000)	4.4
Styrene	312.4
Hydroxyethyl methacrylate	70.3
Butyl acrylate	243.8
Glycidyl methacrylate	215.2
2- Mercaptoethanol	18.4

This pre-emulsion was added to the reactor over a period of 3 h. Simultaneously,
5 the addition of a solution of 4.3 g of sodium formaldehyde sulfoxylate in 131.1 g of water was started. The addition of this mixture was completed in 4 h. After the additions were completed, the batch was kept at 65°C. for an additional 15 min. The batch was then cooled to room temperature (R.T.) and filtered. The polymer dispersion thus obtained had the following properties: solids content 50.0%,
10 particle size 165 nm, pH 8.6. Size exclusion analysis on the polymer gave the following results: Mn 2,661; Mw 6730 (relative to polystyrene standards).

Examples 35-36:

Pigmented single stage waterborne enamel

15 These examples compare comparative Example 35, using a waterborne mixture of epoxy-, hydroxy-, and tertiary-amine-functional polymers, to the present invention (Example 36). Example 36 contains the same waterborne mixture of epoxy-, hydroxy-, and tertiary-amine-functional polymers utilized in Example 35 plus the
20 addition of an anhydride-functional polymer (Example 33) as a co-reactant.

Several commercially available products are used in these examples:

Product	Source	Function	Description
Setal™ 6407 SQ-26	Akzo Nobel Resins	Hydroxy-functional resin	Waterborne Polyester polyol
Setalux™ 8552 AQ-50	Akzo Nobel Resins	Epoxy-functional resin	Waterborne polymer similar to Example 9
Setalux™ 8455 AQ-36	Akzo Nobel Resins	Tertiary-amine- functional resin	Waterborne polymer similar to Example 13
Drewplus™ L-475	Drew International	Defoamer	Blend of mineral oils and silica derivatives
Kronos™ 2310	Kronos	Hiding pigment	Titanium Dioxide
Borchigel™ L75 N	Schoner	Thickener	Polyurethane-based associative thickening agent
Butyl cellosolve	Union Carbide	Solvent	Ethylene glycol butyl ether
Eastman™ TXIB	Eastman Chemicals	Plasticizer	TMPD Diisobutyrate
TEGO Glide™ 410	Tego Chemie	Anti-mar agent	Polysiloxane-polyether copolymer
CAB-O- SPERSE™ CT302C	Cabot	Water repellent	Aqueous dispersion of colloidal silica
TAFIGEL PUR™ 60	Munzing Chemie	Thickener	Polyurethane-based associative thickening agent

The following white single-stage formulations were prepared:

Component	Example 35 Comparative Weight(g) Mole%		Example 36 Present Invention Weight(g) Mole%	
Component A:				
<i>Mix under agitation:</i>				
Setal™ 6407 SQ-26	98.31	9.1%	98.31	7.4%
Drewplus™ L-475	0.31		0.31	
D.I. Water	14.72		14.72	
Kronos™ 2310	173.74		173.74	
Borchigel™ L75 N	2.35		2.35	
Disperse to 7-7.5 Hegman				
<i>Add under slow agitation to the pre-mixed clear base</i>				
<i>Premix the clear base:</i>				
Setalux™ 8455 AQ-36	297.39	38.0%	297.39	30.9%
Eastman™ TXIB	4.80		4.80	
TEGO Glide™ 410 (50% in butyl Cellosolve)	1.84		1.84	
CAB-O-SPERSE™ CT302C	49.87		49.87	
TAFIGEL PUR™ 60 (10% in DI water/butyl cellosolve, 75:25)	11.75		11.75	
D.I. Water	60.81		60.81	
Component B:				
Setalux™ 8552 AQ-50	284.11	52.9%	284.11	42.9%
Component C:				
Resin C (a waterborne anhydride-functional polymer of Example 33)	-----		114.91	18.8%
D.I. Water	-----		22.98	
Methyl amyl ketone	-----		11.49	
Total:	1000.00	100%	1149.38	100%

When ready to use, Components A, B and C can be mixed together in the weight ratios indicated.

- Test panels were prepared by drawing down the formulations with a No.34 Myer bar applicator on 0.025 aluminum panels. This results in a dry film thickness of about 0.8-0.85 mils. MEK double-rubs and König Pendulum Hardness were determined.

The superiority of the present invention is demonstrated by improvements in MEK resistance and better König hardness values shown in Table 5.

Table 5. Properties of Examples 35-36

5

	Example 35 Comparative	Example 36 Present Invention
MEK double-rubs after:		
20 min at 225°F (107°C), after cool-down	28	56
plus 1 day RT*	58	90
20 min at 250°F (121°C), after cool-down	60	164
König Pendulum Hardness after:		
20 min at 225°F (107°C), after cool-down	132	149
plus 1 day RT	148	161
20 min at 250°F (121°C), after cool-down	147	166

* RT= Room Temperature, ambient conditions.

10 The above results clearly demonstrate the outstanding solvent resistance and hardness development of the present invention (Example 36) in comparison with comparative Example 35.

Examples 37-38:

Clearcoat enamel formulations

15

These examples compare comparative Example 37 where a mixture of epoxy-, hydroxy-, and anhydride-functional compounds are catalyzed by a small amount of a tertiary-amine catalyst (benzyl dimethylamine- 0.5% on total solids) to the

present invention (Example 38) utilizing a tertiary-amine-functional polymer as a co-reactant.

Several commercially available products are used in this example:

Product	Source	Functionality	Comments
ERL™-4221	Dow Chemical	Epoxy	3,4-Epoxycyclohexyl-methyl 3,4-Epoxy-cyclohexane-carboxylate
Setal™ 26-1688	Akzo Nobel Resins	Hydroxyl	Polyester polyol

5

The following clearcoat formulations were prepared:

Component	Example 37 Comparative Weight(g) Mole%		Example 38 Present Invention Weight(g) Mole%	
Component A:				
ERL™-4221	41.2	42.8%	41.1	42.6%
Setal™ 26-1688	98.8	28.6%	98.8	28.4%
Xylene	60.4		60.0	
Component B:				
Resin B (tertiary amine-functional polymer, Example 32)	None		4.7	0.6%
Catalyst: Benzyl dimethylamine	0.96	(0.5% on solids)	None	
Component C:				
Resin C (anhydride-functional polymer, Example 4)	143.4	28.6%	143.3	28.4%
Total:	344.76	100%	347.9	100%

When ready to use, Components A, B and C can be mixed together in the weight ratios indicated.

10

Test panels were prepared by drawing down the formulations with a No.40 Myer bar applicator on 16 gauge steel panels. This results in a dry film thickness of

about 1.0-1.2 mils. MEK double-rubs and König Pendulum Hardness were determined.

The superiority of the present invention is demonstrated by improvements in MEK resistance and better hardness values shown in Table 6.

5 Table 6. Properties of Examples 37-38.

	Example 37 Comparative	Example 38 Present Invention
MEK double-rubs after:		
20 min at 300°F (149°C)	17	90
König Pendulum Hardness after:		
20 min at 300°F (149°C)	70	125

The invention is further illustrated by the following claims, which, however,
10 do not limit the scope thereof.

CLAIMS:

1. A reactive non-isocyanate coating composition obtained by mixing epoxy, tertiary amine, anhydride, hydroxy- and, optionally, acid-functional compounds, wherein:

the tertiary amine-functional compound is an oligomeric or polymeric tertiary amine, with or without other functional groups, and is present in an amount greater than 0.5 mole %,

the tertiary amine-functional groups are reactive with the epoxy-functional groups of the epoxy-functional compound, and the anhydride-functional compound is a monomeric, oligomeric or polymeric cyclic anhydride.

2. The composition of claim 1, wherein the anhydride-functional compound is an oligomeric or polymeric anhydride having two or more anhydride groups per molecule.

3. The composition of claim 1 or 2, wherein the tertiary amine-functional compound is an oligomeric or polymeric tertiary amine having two or more tertiary amine groups per molecule.

4. The composition of any one of claims 1-3, wherein the epoxy-functional compound is an oligomeric or polymeric epoxy having two or more epoxy-functional groups per molecule.

5. The composition of any one of claims 1-4, wherein the composition further comprises an acid-functional compound.

6. The composition of claim 5, wherein the tertiary amine- and acid-functional compounds are combined in a first polymer comprising tertiary amine- and acid-functional groups; the epoxy- and hydroxy-functional compounds are combined in a second polymer comprising epoxy- and hydroxy-functional groups, and the anhydride-functional compound is in the form of a third polymer.

7. The composition of any one of claims 1 to 4, wherein the tertiary amine-functional compound is in the form of a first polymer, the epoxy-functional compound is in the form of a second polymer, the anhydride-functional compound is in the form of a third polymer, and the hydroxy-functional compound is in the form of a fourth polymer or made by introducing a hydroxy-functional group on the first or second polymer.

8. The composition of claim 7, wherein the composition further comprises an acid-functional compound and the acid-functional compound is made by introducing an acid-functional group on the first or third polymer.

9. The composition of any one of claims 1 to 8, wherein the composition is a waterborne or solvent-borne composition.

10. The composition of any one of claims 1 to 8, wherein the tertiary amine-functional compound is an acrylic copolymer, based on dimethylaminoethyl methacrylate, the epoxy-functional compound is an acrylic copolymer containing glycidyl methacrylate, or a cycloaliphatic epoxy, the anhydride-functional compound is a monomeric, oligomeric or polymeric cyclic diacid anhydride, a copolymer of maleic anhydride, styrene and acrylic monomers, or a mono-anhydride and the mono-anhydride is a dodecenyl succinic anhydride.

11. The composition of any one of claims 1 to 10, wherein anhydride-functional groups of the anhydride-functional compound are reactive with hydroxyl-functional groups of the hydroxy-functional compound.

12. A coating system having at least three components which are combined to make a coating composition comprising:

a component 1 being an oligomeric or polymeric tertiary amine-functional compound,

a component 2 being a monomeric, oligomeric, or polymeric anhydride-functional compound,

a component 3 being an oligomeric or polymeric epoxy-functional compound, and, the system also comprising a component 4 being a hydroxy-functional compound, the hydroxy-functional compound being a separate component or being combined with the oligomeric or polymeric tertiary amine-functional compound 1 or the epoxy-functional compound 2.

13. The coating system of claim 12, further comprising:

a component 5 being an acid-functional compound, the acid-functional compound being a separate component or being combined with the oligomeric or polymeric tertiary amine-functional compound 1, the anhydride-functional compound 2, or the hydroxy-functional compound 4.

14. A substrate coated with the coating composition of any one of claims 1 to 11, or with a coating composition made from the coating system of claim 12 or 13.