WATER BORNE CURING AGENT COMPOSITION, COMPRISING A PREREACTED SURFACTANT COMPOSITION, FOR SELF-CURING EPOXY RESINS AT AMBIENT OR SUB-AMBIENT TEMPERATURES

This invention is related to a surfactant composition and to water borne, self emulsifiable, stable curing agent compositions for epoxy resins, curable at ambient and sub-ambient temperatures in the absence of external catalysts/accelerators. The invention is also directed to methods of application and manufacture, as well as to the cured products made thereby.

There has long been a desire to formulate a curing agent which is essentially free of volatile organic compounds (VOC's), which are self emulsifiable and curable at a wide range of temperatures in the absence of external accelerators if possible.

Many of the current water borne epoxy resins and curing agents are plagued with the problem of poor film properties because the surfactants tend to migrate to the surface during the cure of the resin system. Thus, it would be desirable to provide a curing agent system containing a surfactant which does not migrate during cure, that is, a self emulsifiable system which does not require salting the surfactant or using plasticizers to stably disperse the curing agent in water.

In addition to providing a self emulsifiable water borne curing agent, the curing agent should be readily compatible with a water borne epoxy resin in order to make a coating having good mechanical properties and weatherability. A water borne curing agent that does not have good compatibility with the epoxy resin will

not coalesce well when applied onto a substrate. The problem of compatibility is more acute where the curing agent primary amine groups have been converted to secondary amine groups to reduce the blooming or hazing phenomena.

Further, in view of the continuous need to provide curing agents which are environmentally friendly, the self emulsifiable curing agent should contain little or no VOC's, that is, be dispersed in water or other non-VOC, without the need to use co-solvents to solubilize the curing agent. Moreover, the surfactant used to disperse the curing agent should be effective to disperse large quantities of the curing agent to provide a high solids level. Of course, the water borne curing agent should also be stable, at least long enough to mix, store, ship and apply.

It is also desirable that the water borne curing agent cure water borne epoxy resins at ambient temperatures, preferably without the use of external accelerators or catalysts. This would reduce the overall cost of the system and avoid the potential for migration of catalyst from the coating. Thus, the curing agent should be sufficiently reactive so that accelerators are not needed for room temperature cure, but not excessively reactive that on loses the pot life needed for applying or working with the system.

The water borne curing agent composition of the invention is a solid phase dispersed in a continuous phase, the continuous phase comprising water, the solid phase comprising a curing agent composition and a surfactant composition. The dispersion can be a suspension, emulsion, or a colloidal dispersion. The aqueous continuous phase can contain other liquids in

admixture, but is preferably free of any VOC's and free of any cosolvents. By an continuous phase that is essentially free of VOC's is meant that 5 wt% or less of the water borne curing agent composition is a VOC.

The aqueous dispersion of the invention is also stable, meaning that there is no evidence to the naked eye that the solid and liquid phases have phase separated into discrete layers at 30 days of storage at 23 °C without agitation or disturbance. Preferably, the water borne compositions do not exhibit phase separation even at 2 months, more preferably at 6 months of storage.

Another attribute of the invention is that the water borne curing agent of the invention can be made stable without the use of plasticizers or organic acids typically used to make salt the curing agent, that are usually present in water borne compositions. The water borne curing agent composition of the invention is self emulsifiable, meaning that the curing agent has the capacity to stably disperse in water at a solids level of at least 40 wt%, preferably 50 wt% or more, in the absence of solvents, plasticizers, or salting organic acids.

A further attribute of the invention is that the water borne compositions of the invention cure well and are compatible with water borne epoxy resins at ambient temperatures in the absence of external cure accelerators. The specular gloss readings taken from samples of the water borne curing agent compositions of the invention reacted with water borne epoxy resins indicate that the curing agent compositions of the invention sufficiently cured the epoxy resin component at ambient temperature.

The surfactant composition comprises the reaction product of an a) a phenolic compound, substituted with at least one carboxyl group and at least one hydrocarbyl group having at least 1 carbon atom, b) a polyamine compound having at least two primary amine groups, c) a reactive surfactant, and optionally d) a monoglycidyl, monocarboxylic acid or monoisocyanate capping agent.

According to one of the preferred groups of embodiments (I) of the present invention, said surfactant composition comprises a reaction product of the components a), b), c) and optionally d) and in addition a polyepoxide compound e).

According to another of the preferred groups of embodiments (II) of the present invention, said surfactant composition comprises the reaction product of a substituted aryl amidopolyamine, a d) monoglycidyl or monocarboxylic acid capping agent, and a c) reactive surfactant, said substituted aryl amidoamine comprising the reaction product of:

a) a phenolic compound substituted with at least one carboxyl group and at least one hydrocarbyl group having at least 1 carbon atom, and

b) a polyamine compound having at least two primary amine groups;

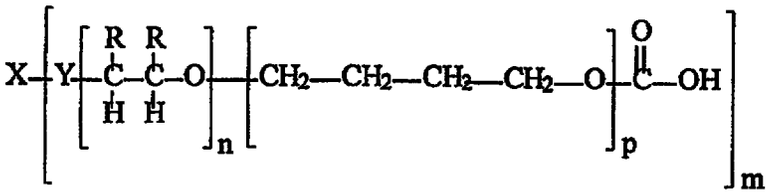
said reactive surfactant comprising a functional moiety reactive with secondary amines and a hydrophilic moiety of a nature and length effective to disperse the curing agent in water.

According to both groups of embodiments (A and B) the functional moiety in the reactive surfactant comprises an epoxide group, a carboxylic acid group or anhydrides thereof, an isocyanate group, or mixtures thereof; and the hydrophilic moiety in the reactive

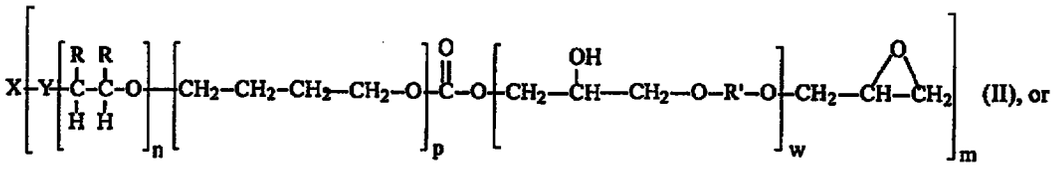
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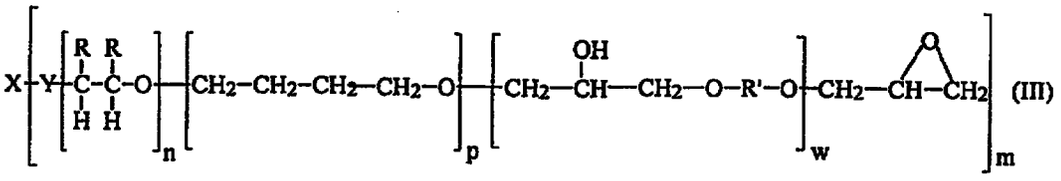
surfactant comprises a polyoxyalkylene monool or polyol residue. In a preferred embodiment, the reactive surfactant comprises a compound represented by one of the following formulas:



(I), or



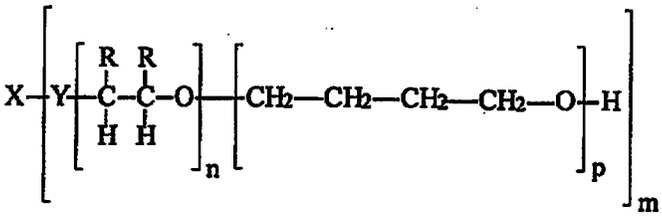
(II), or



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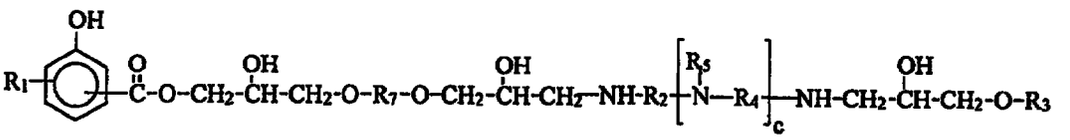
wherein X represents an initiator molecule residue, the initiator having a functionality of from 1 to 8; Y represents an oxygen or nitrogen atom; each of the R's independently represent a hydrogen, an C_1-C_{16} alkyl, aryl, or alkaryl group, provided that at least one R is a hydrogen; R' represents an epoxy resin residue comprising a divalent aliphatic group, a divalent cycloaliphatic group, a divalent aryl group, a divalent arylaliphatic group, or a divalent alkaryl group, each having from 2 to 1000 carbon atoms; m represents a real number from 1 to 8; n and p represent the number of repeating units of oxyalkylene groups effective to stably disperse the curing agent composition in water

and ranging from 0 to 20; and w represents the number of epoxy glycidyl ether units, ranging from 0 to 20. A typical polyoxyalkylenemonool or polyol can be represented by the formula:



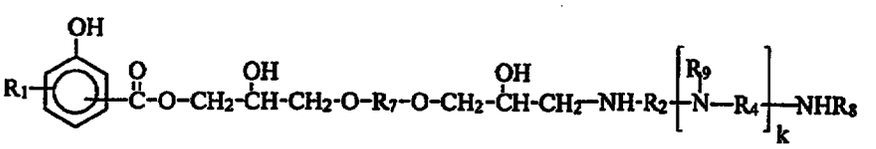
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In one group of embodiments (A), the surfactant composition comprises a compound represented by at least one of the following formulas:



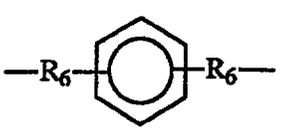
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or



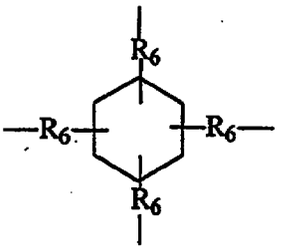
(VI)

wherein R_1 is a branched or unbranched, substituted or unsubstituted, monovalent hydrocarbyl group having at least on carbon atom; R_2 and R_4 each independently represent a branched or unbranched, substituted or unsubstituted, divalent hydrocarbyl group having 2-24 carbon atoms, or



(VII)

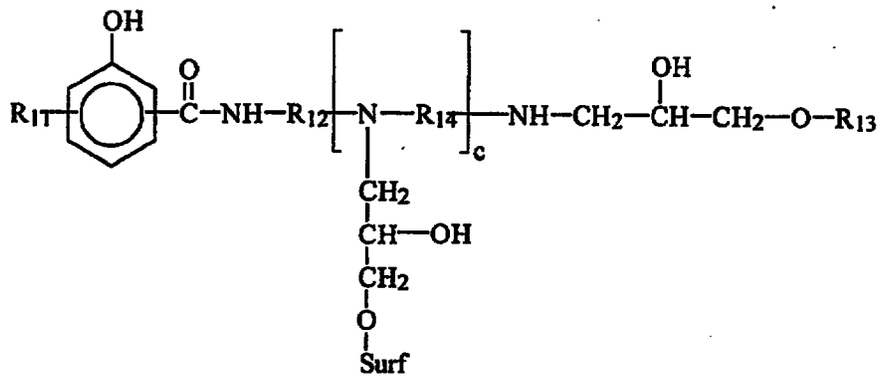
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(VIII)

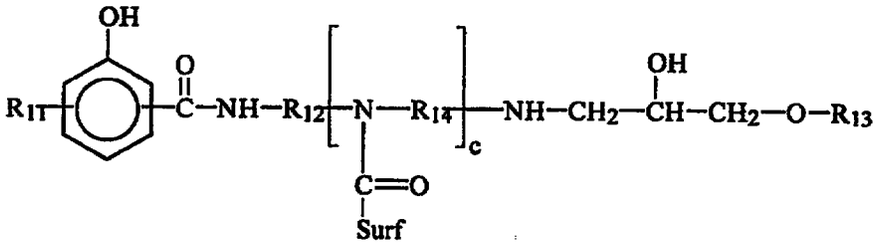
R_6 represents a branched or unbranched, substituted or unsubstituted, divalent hydrocarbyl group having 2-24 carbon atoms; R_3 is a branched or unbranched, substituted or unsubstituted, monovalent hydrocarbyl having 1-24 carbon atoms, an aryl group, an alkaryl group, or an aralkyl group; R_7 is the residue of said e) polyepoxide compound; R_5 and R_9 are each independently hydrogen, or a branched or unbranched, substituted or unsubstituted, alkyl group or alkaryl group or cycloaliphatic group, or the residue of said d) reactive surfactant; R_8 is the residue of said d) reactive surfactant; c represents an integer from 1-10; and k represents an integer from 0-10; provided that at least one R_5 group is said the residue of said c) reactive surfactant.

In another group of embodiments (B), the surfactant composition comprises a compound represented by at least one the following formulas:



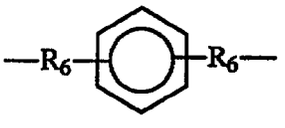
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or



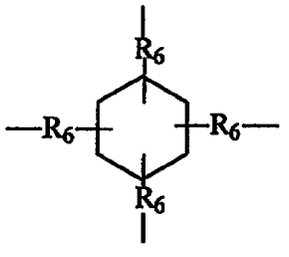
(X)

wherein R_{11} is a branched or unbranched, substituted or unsubstituted, monovalent hydrocarbyl group having at least one carbon atom; R_{12} and R_{14} each independently represent a branched or unbranched, substituted or unsubstituted, divalent hydrocarbyl group having 2-24 carbon atoms, or



(VII)

or



(VIII)

R_6 represents a branched or unbranched, substituted or unsubstituted, divalent hydrocarbyl group having 2-24 carbon atoms; R_{13} is a branched or unbranched, substituted or unsubstituted, monovalent hydrocarbyl having 1-24 carbon atoms, an aryl group, an alkaryl group, or an aralkyl group; c represents an integer from 0-10; and Surf represents the c) reactive surfactant residue; provided that when c=0, the -CO-Surf group and the $-CH_2-CHOH-CH_2-O$-Surf group are bonded to the nitrogen atom farthest from the depicted amide group.

In a process for the preparation of the group of surfactant embodiments A, the phenolic acid compound is reacted with the polyepoxide compound to produce a substituted aromatic glycidyl ester compound, wherein the substituted aromatic glycidyl ester compound is reacted with the polyamine compound to make a substituted aromatic glycidyl ester - amine adduct, followed by

i) combining and reacting the d) capping agent with said substituted aromatic glycidyl ester - amine adduct to form a capped substituted aromatic glycidyl ester-amine adduct, followed by combining and reacting the c) reactive surfactant, or

ii) combining and reacting the substituted aromatic glycidyl ester-amine adduct with the c) reactive surfactant.

The curable two component systems, a water borne epoxy resin and a water borne curing agent, can be cured to form coatings and in flooring, casting, crack or defect repair, moulding, adhesives, potting, filament winding, encapsulation, structural and electrical laminates, composites and the like.

In a process for the preparation of the group of surfactant embodiments B, the surfactant composition is made by reacting an a) substituted aryl amidopolyamine with a d) monoglycidyl capping agent and a c) reactive surfactant. The substituted aryl amidopolyamine is made by reacting an ai) phenolic compound substituted with at least one carboxyl group and at least one hydrocarbyl group having at least 1, and preferably 12 or more, more preferably 14 or more carbon atoms, and an aii) an aliphatic polyamine compound having at least two primary amine groups.

The structure of the phenolic compound is an aromatic ring to which is covalently bonded at least one hydroxyl group, at least one hydrocarbyl group, and at least one carboxyl group. Usually and preferably, the structure of the phenolic compound will contain only one hydroxyl group and one carboxyl group bonded to the aromatic ring. However, it is rare if not impossible to commercially acquire a phenolic compound which is so pure that it contains only one species. Commercially available phenolic compounds usually contain a mixture of species, such as mono and di carboxyl substituted phenolics. Thus, while the preferable embodiment is one in which the phenolic compound contains only one of each group bonded to the aromatic ring, this embodiment includes a phenolic which contains a mixture of species in which the predominant (>70 mole percent) species has only one carboxyl group and one hydroxyl group bonded to the aromatic ring.

One of the substituents on the aromatic ring of the phenolic compound is the hydrocarbyl group. While the hydrocarbyl group can comprise a wide variety of structures and atoms, it must have a predominantly

hydrocarbon character. Included within the meaning of a hydrocarbyl group are the alkyl or alkenyl groups, the aliphatic substituted aromatic or alicyclics, or the aromatic or alicyclic substituted alkyls or alkenyls. Each of these groups may be branched or unbranched. The phenolic compound preferably contains at least 50 mole% species which have only one hydrocarbyl substituent.

The substituent on the substituted aryl amido-polyamine is at least one hydrocarbyl group having at least one carbon atom. Longer chain hydrocarbyl groups are preferred. All else remaining equal, a curing agent having longer chain hydrocarbyl substituents, i.e. 8 or more and preferably greater than 12, most preferably 14 or more, tend to be more hydrophobic than the curing agents having short chain hydrocarbyl groups on the order of 1-7 carbon atoms. In many applications, the hydrophobic character of the hydrocarbyl substituent is desirable to improve the compatibility of the curing agent with the epoxy resin component. Further, long chain hydrocarbyl substituents are somewhat more flexible than their shorter chain counterparts, thus lowering the glass transition temperature of the curing agent. It is desirable to have a curing agent with a lowered glass transition temperature to improve its flow properties in low temperature curing conditions. Thus, the most preferred hydrocarbyl groups are those having 14 or more carbon atoms. Although there is no particular upper limit on number of carbon atoms, the most common number of carbon atoms used within this invention will be 14-24, most preferably from 14-18, although hydrocarbons with up to 36 carbon atoms are also available.

Of the types of hydrocarbyl substituents, the alkyls are preferred. These can be branched or unbranched,

preferably unbranched or having no more than 1 branch per 6 backbone carbon atoms. Examples of alkyl substituents having at least 8 carbon atoms include octyl, nonyl, decyl, isodecyl, dodecyl, pentadecyl, eicosyl, triacontyl and the like, as well as radicals derived from substantially saturated petroleum fractions, olefin polymers and highly refined white oils or synthetic alkanes.

Other types of hydrocarbyl groups which are suitable include substituted hydrocarbyl groups; that is, groups containing non-hydrocarbon substituents which do not alter the predominantly hydrocarbon character of the group. Examples are halo, nitro, cyano, ether, carbonyl, and sulfonyl groups. Also included are hetero atoms which are atoms other than carbon present within a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms include, for example, nitrogen, oxygen, and sulphur. Further included within the meaning of the hydrocarbyl group are the alkoxy compounds.

Preferably, no more than an average of one substituent or hetero atom will be present for each 10 carbon atoms in the hydrocarbyl group, and most preferably, the hydrocarbyl group does not contain any hetero atoms or substituents.

The phenolic compound may contain more than one hydrocarbyl substituent on its aromatic ring. The dihydrocarbyl phenolic compounds have a long chain hydrocarbyl of 14 or more carbon atoms and a short chain hydrocarbyl of 1-4 carbon atoms attached to the aromatic ring, or both of the hydrocarbyls may be long chain. As noted above, however, preferably greater than 50 mole% of the species contain only one hydrocarbyl substituent.

The substituted aryl amidopolyamines may contain more than one hydrocarbyl substituent on the aromatic ring of the phenolic compound. The dihydrocarbyl substituted aryl amidopolyamines may have a long chain hydrocarbyl of 14 or more carbon atoms and a short chain hydrocarbyl of 1-4 carbon atoms attached to the aromatic ring of the phenolic compound, or both of the hydrocarbyls may be long chain. As noted above, however, preferably greater than 50 mole%.

The phenols on which the hydrocarbyl and carboxyl groups are situated, are aromatic compounds containing at least one, and preferably one, hydroxyl group. Examples are phenol, α- or β- naphthols, resorcinol, hydroquinone, 4,4'-dioxydiphenyl, 4,4'-dioxydiphenylether, 4,4'-dioxydiphenylsulfone, 4,4'-dioxydiphenylmethane, the condensation products of phenol and formaldehyde known as novolacs, and bis(4-hydroxyphenyl) alkyls or ethers or sulfones optionally substituted with alkyl groups on the aromatic rings. Phenol is preferred.

To substitute the hydroxyl aromatic compound with the hydrocarbyl group, a hydrocarbon-based compound of the hydrocarbyl group as mentioned above is reacted with the hydroxyl aromatic compound at a temperature of 50-200 °C in the presence of a suitable catalyst such as aluminium chloride, boron trifluoride or zinc chloride.

The phenolic compound also contains at least one carboxyl group as a substituent, and preferably only one carboxyl group per aromatic ring. The carboxyl group is bonded directly to the aromatic phenolic ring, or indirectly to the ring through an aliphatic chain. Preferred, however, is a carboxyl group bonded directly to the aromatic ring of the phenolic compound at the

ortho or para positions to the phenolic hydroxyl group. Further, within the meaning of a carboxyl group are the alkyl esters and anhydrides of the carboxyl substituents.

Examples of the carboxyl groups bonded to the phenolic aromatic ring are those derived from carboxylic acids containing 0-24 carbon atoms, not counting the carboxylic acid carbon. The carboxylic acids from which the substituents are derived include -formic acid (a -carboxy acid), -acetic acid, -proprionic acid, or -stearic acid substituents. A particularly preferred carboxyl group is a carboxy acid in view of its high reactivity with amines.

The phenolic compound containing the carboxyl and the hydrocarbyl groups can be prepared by methods which are known in the art as the "Kolbe-Schmitt reaction," which comprises reacting a salt, preferably an alkali metal salt, of the hydrocarbyl substituted phenol with carbon dioxide and subsequently acidifying the salt thus obtained. The conditions of the carbonation reaction are likewise well known to those skilled in the art. It may be carried out at atmospheric or superatmospheric pressure in a substantially inert, non-polar liquid diluent.

A particularly preferred phenolic compound is a hydrocarbyl substituted salicyclic acid. This phenolic compound is a good building block toward producing a curing agent which has good flow, reactivity, and compatibility with epoxy resins at low cure temperatures in the absence of external accelerators/catalysts, and a good balance of mechanical properties and water, corrosion and humidity resistance properties.

In a more preferred embodiment, the phenolic compound used in the invention is a salicyclic acid substituted with a 14-18 linear carbon alkyl group located at the o- or p- position to the phenolic hydroxyl group. The preparation of alkyl substituted salicyclic acids is described in US Patent No. 3,013,868.

To manufacture the substituted aryl amidopolyamine, the phenolic compound described above is reacted with a polyamine compound having at least two primary amine groups at an elevated temperature, suitably at a temperature of from 150 °C to 160 °C for a time sufficient to substantially complete the reaction, usually from 4 to 12 hours. The ingredients can be mixed together and reacted, but preferably, the phenolic compound should be added to the polyamine compound so as to reduce the possibility of reacting both of the primary amine groups on the polyamine compound with the phenolic compound. This reaction may be carried out in the presence of absence of solvents or catalysts, typically in the presence of a solvent and in the absence of a catalyst. If a catalyst is employed, one could use triphenylphosphite. It is advisable not to let the reaction temperature rise too much above 170 °C for an extended period of time in order to avoid de-carboxylating the phenolic compound and the resultant production of free phenolic compounds in the reaction mixture. To drive the reaction to completion, vacuum may be applied during the course of the reaction or towards the tail end of the reaction.

Preferably, at least one primary nitrogen group equivalent of polyamine is reacted per carboxyl group equivalent on the phenolic compound, and more preferably

the polyamine is reacted with the phenolic compound at a molar excess, such as at a molar ratio of 1.25:1 or more, in order to react out the all the carboxyl groups to form amide groups wherever carboxyl groups appear on the phenolic compound. While molar ratios of less than 1:1 are tolerable, the object of providing a reactive curing agent at low temperature cure conditions which is storage stable and compatible with epoxy resins is best achieved if an molar equivalent or excess of the polyamine is used. Once the amine reaction onto the phenolic compound and the reaction is complete, the excess amine, if any, should be vacuum distilled off, typically at 20in.Hg to 30in.Hg for 30 to 480 minutes.

Other groups related to the amide group formed by the reaction between the carboxyl group and the polyamine that are within the meaning of the term amide include the imides and the amidines.

To manufacture the substituted aromatic glycidyl ester composition to be used according to the group of embodiments A, the phenolic acid described above is reacted with an polyepoxide at an elevated temperature, typically from 140 °C to 180 °C, for a time sufficient to substantially complete the reaction, usually from 1 to 8 hours. It is advisable not to let the reaction temperature rise too much above 170 °C-180 °C for an extended period of time in order to avoid the possibility of de-carboxylating the phenolic compound, which would result in the production of free phenolic compounds in the reaction mixture. The reaction can be conducted at any pressure ranging from a partial vacuum to superatmospheric pressure. To drive the esterification reaction between the carboxyl group on the phenolic compound and the polyepoxide compound to

completion, it is preferred to apply a partial vacuum either during the course of the reaction or towards the tail end of the reaction. The reaction is substantially completed when free acid can no longer be detected in the composition. The ingredients can be mixed together and subsequently reacted, but preferably, the phenolic acid is added to the polyepoxide compound so as to reduce the possibility of reacting both of the oxirane groups on the polyepoxide compound with the phenolic acid.

The reaction between the polyepoxide compound and the phenolic acid are suitably carried out at molar ratios of at least 1:1, preferably greater than 1:1 such as at least 2:1, and even 3:1 on up. It is desirable to use a molar excess of the polyepoxide compound so that one of the oxirane groups on the polyepoxide compound is free to react with the polyamine compound and does not react with further phenolic acids. If a stoichiometric amount of the phenolic acid is added to the polyepoxide compound such as at a molar ratio of polyepoxide to phenolic acid of 0.5:1 or less (the stoichiometry proceeding upon the assumption that the phenolic acid has only one functional group, the acid group, and a diepoxide is used), then both of the oxirane groups will be consumed by the acid group on the phenolic compound. Therefore, a stoichiometric excess of oxirane groups (>0.5:1) is desired to ensure that the substituted aromatic glycidyl ester compound has free oxirane groups available for reaction with the polyamine compound.

The reaction between the phenolic acid and the polyepoxide compound may be carried out in the presence or absence of solvents or catalysts, typically in the presence of both. Suitable solvents include alcohols,

ketones, esters, ethers of hydrocarbons. Examples of suitable solvents are butanol, methyl isobutyl ketone, toluene, ethylglycol acetate, xylene, benzyl alcohol, phthalic acid esters of monohydric alcohols, e.g. n-butanol, amylalcohol, 2-ethylhexanol, nonanol, benzyl alcohol, gamma-butyrolactone, delta-valerolactone, epsilon-caprolactone, lower and higher molecular weight polyols, e.g. glycerol trimethylol-ethane or -propane, ethyleneglycol, and ethoxylated or propoxylated polyhydric alcohols, either individually or in admixture.

If a catalyst is employed, one could use a Lewis acid, metal salts, and bases. Examples include triethylamine, triethylamine, benzyldimethylamine, tris(dimethylaminomethyl)phenol, dimethylethanolamine, n-methymorpholine, benzyl trimethyl ammonium chloride, ethyl triphenyl phosphonium salts, tetrabutyl phosphonium salts, and stannous salts of carboxylic acids. Typical amounts of catalyst used range from 0.1 to 100 ppm.

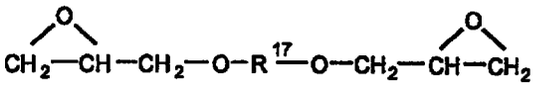
The polyepoxide used in the invention is any polyepoxide having an average of 1.5 or more oxirane groups per molecule, preferably 1.7 or more oxirane groups. The polyepoxide compounds can be monomeric or polymeric, saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heteroaromatic and may be substituted, if desired, with other substitutents in addition to the epoxy groups with, for example, hydroxyl groups or halogen atoms such as bromine.

Suitable polyepoxide compounds are the reaction products of polyphenols and epihalohydrins, polyalcohols and epihalohydrins, amines and epihalohydrins, sulphur

containing compounds and epihalohydrins, polycarboxylic acids and epihalohydrins or mixtures thereof.

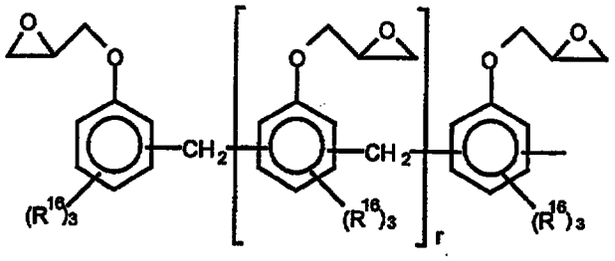
Preferred polyepoxide compounds include, but are not limited to, any one of those represented by the formulas:

or



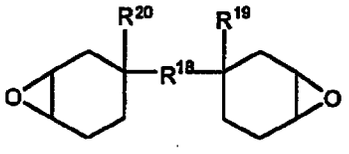
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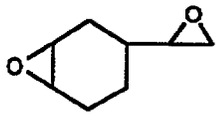


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(XIII) or

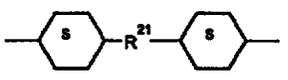


(XIV)

wherein r is a real number from about 0 to about 6, R^{17} is a divalent aliphatic group, a divalent cycloaliphatic group, a divalent aryl group, a polyoxyalkylene group, or a divalent arylaliphatic group, R^{16} is independently a hydrogen or a C_1-C_{10} alkyl group, R^{18} is a divalent aliphatic group optionally containing ether or ester group(s) or together with R^{19} or R^{20} form a spiro ring optionally containing heteroatoms,

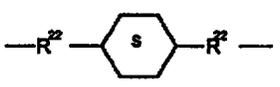
and R^{19} and R^{20} are independently hydrogen or R^{19} or R^{20} together with R^{18} form a spiro ring optionally containing heteroatoms such as oxygen.

R^{17} can be a divalent cycloaliphatic group having the formula:



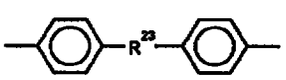
(XV)

or



(XVI)

wherein R^{21} and R^{22} are each independently an alkylene group, or a divalent arylaliphatic group having the formula



(XVII)

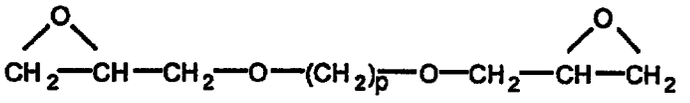
wherein R^{23} is an alkylene group.

For the polyepoxide compound having a nominal functionality of two or more, the epoxy compound is preferably a diglycidyl ether of a dihydric phenol, diglycidyl ether of a hydrogenated dihydric phenol, an aliphatic glycidyl ether, epoxy novolac or a cycloaliphatic epoxy.

Diglycidyl ethers of dihydric phenols can be produced, for example, by reacting an epihalohydrin with a dihydric phenol in the presence of an alkali. Examples of suitable dihydric phenols include: 2,2-bis(4-hydroxyphenyl) propane (bisphenol-A); 2,2-bis(4-

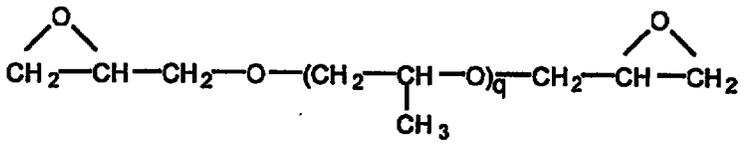
hydroxy-3-tert-butylphenyl) propane; 1,1-bis(4-hydroxyphenyl) ethane; 1,1-bis(4-hydroxyphenyl) isobutane; bis(2-hydroxy-1-naphthyl) methane; 1,5-dihydroxynaphthalene; 1,1-bis(4-hydroxy-3-alkylphenyl) ethane and the like. Suitable dihydric phenols can also be obtained from the reaction of phenol with aldehydes such as formaldehyde (bisphenol-F). Diglycidyl ethers of dihydric phenols includes advancement products of the above diglycidyl ethers of dihydric phenols with phenolic compounds such as bisphenol-A, such as those described in U.S. Patent Nos. 3,477,990 and 4,734,468.

Diglycidyl ethers of hydrogenated dihydric phenols can be produced, for example, by hydrogenation of dihydric phenols followed by glycidation with epihalohydrin in the presence of a Lewis acid catalyst and subsequent formation of the glycidyl ether by reaction with sodium hydroxide. Examples of suitable dihydric phenols are listed above.



(XVIII)

and aliphatic glycidyl ethers can be produced, for example, by reacting an epihalohydrin with an aliphatic diol in the presence of a Lewis acid catalyst followed by conversion of the halohydrin intermediate to the glycidyl ether by reaction with sodium hydroxide. A representative formula is:



(XIX)

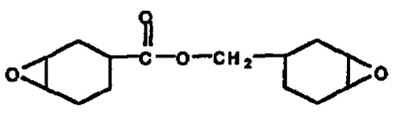
wherein p is an integer from 2 to 12, preferably from 2 to 6; and q is an integer from 4 to 24, preferably from 4 to 12.

Examples of suitable aliphatic glycidyl ethers include for example, diglycidyl ethers of 1,4 butanediol, neopentyl glycol, cyclohexane dimethanol, hexanediol, polypropylene glycol, and like diols and glycols; and triglycidyl ethers of trimethylol ethane and trimethylol propane.

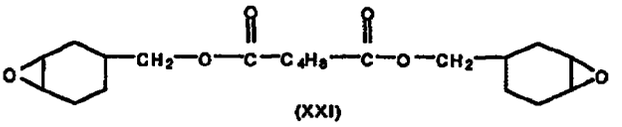
Epoxy novolacs can be produced by condensation of formaldehyde and a phenol followed by glycidation by epihalohydrin in the presence of an alkali. The phenol can be for example, phenol, cresol, nonylphenol and t-butylphenol. Examples of the preferred epoxy novolacs include those corresponding to the formula (XII) above. Epoxy novolacs generally contain a distribution of compounds with a varying number of glycidated phenoxymethylene units, r. Generally, the quoted number of units is the number closest to the statistical average, and the peak of the distribution.

Cycloaliphatic epoxies can be produced by epoxidizing a cycloalkene-containing compound with greater than one olefinic bond with peracetic acid. Examples of the preferred cycloaliphatic epoxies include those corresponding to the formula (XIV) above. Examples of cycloaliphatic epoxies include, for example, 3,4-epoxycyclo-hexylmethyl-(3,4-epoxy)-cyclohexane carboxylate, dicycloaliphatic diether

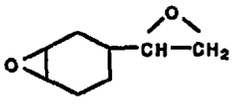
diepoxy [2-(3,4-epoxy)cyclohexyl-5,5-spiro(3,4-epoxy)-cyclohexane-m-dioxane], bis(3,4-epoxycyclohexyl-methyl)adipate, bis(3,4-epoxycyclohexyl)adipate and vinylcyclohexene dioxide [4-(1,2-epoxyethyl)-1,2-epoxycyclohexane]. Cycloaliphatic epoxies include compounds of the formulas:



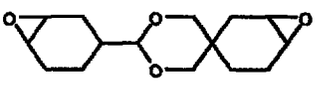
(XX)



(XXI)



(XXII)

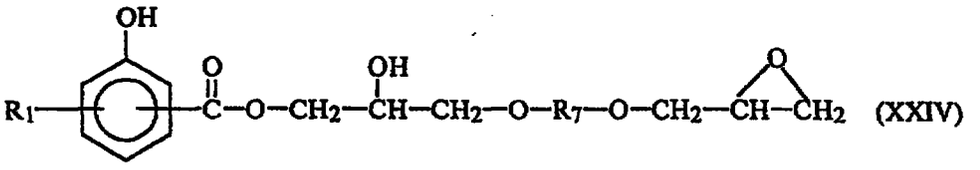


(XXIII)

Commercial examples of the preferred epoxy compounds having a nominal functionality of two or more include, for example, EPON Resins DPL-862, 828, 826, 825, 1001, EPONEX Resin 1510, HELOXY Modifiers 107, 67, 68, and 32 (EPON, EPONEX and HELOXY are trademarks); all available from Shell Chemical Company and Union Carbide Epoxy Resins ERL-4221, -4289, -4299, -4234 and -4206.

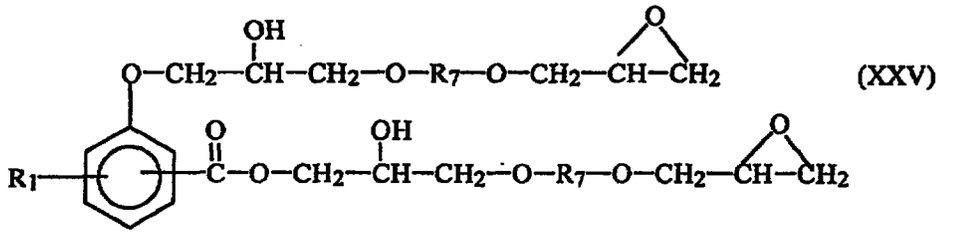
The reaction between the phenolic acid compound and the polyepoxide compound will produce a variety of species depending upon the particular phenolic acid functional sites which undergo reaction. The following reaction scheme represents two species produced between phenolic acid - polyepoxide reaction, where all of the

carboxylic acid groups on the phenolic acid compound have been reacted:



(XXIV)

and



(XXV)

wherein R_1 is the hydrocarbyl substituent on the phenolic acid compound, and R_7 is the polyepoxide residue.

Once the substituted aromatic glycidyl ester composition is made, it is reacted with

i) the b) polyamine compound, the d) monoglycidyl capping agent, and the c) reactive surfactant, in the stated sequence; or

ii) a pre-reaction product of at least one equivalent of b) polyamine per equivalent of the c) reactive surfactant, followed by reaction onto the substituted glycidyl ester compound, in which case no capping agent is needed.

However, combining the polyamine and monoglycidyl capping agent in mixture with the substituted glycidyl ester compound, followed by reaction with the c) reactive surfactant, is also suitable for the purposes of the invention.

In the case where the surfactant composition is made in-situ, during the manufacture of the curing agent composition, the surfactant composition can be made by:

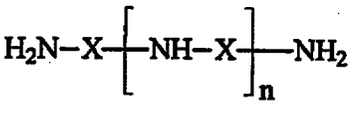
iii) reacting the reactive surfactant with a stoichiometric excess of the curing agent composition, where the curing agent composition comprises an end capped substituted aromatic glycidyl ester-amine adduct comprising the reaction product of said a), e), c), and d); or

iv) pre-reacting the reactive surfactant with the b) polyamine compound, followed by reaction with a molar excess of the substituted aromatic glycidyl ester compounds, followed by reacting at least a molar equivalent amount, preferably a large molar excess, of a second portion of b) polyamine compound with the unreacted substituted aromatic glycidyl ester compounds to make a substituted aromatic glycidyl ester-amine adduct, and end capping at least a portion of unreacted primary amine groups remaining on said adduct with the d) capping agent.

Regardless of whether the surfactant composition is made and isolated as such, or made in situ, preferably at least one mole of the polyamine compound is reacted per mole of the substituted aromatic glycidyl esters, and more preferably the polyamine is reacted with the substituted aromatic glycidyl esters at a molar excess, such as at a molar ratio of 1.25:1 or more, more preferably 2:1 or more, in order to react out the all the oxirane groups and provide primary amino group termination. The reaction conditions are much like those described above with relation to the phenolic acid and the polyepoxide compound, except that typically no catalysts are needed. The temperature can range from

100 °C to 230 °C, with the higher end of the temperature range initiated when vacuum distillation is applied. The substituted aromatic glycidyl ester composition is preferably added to the polyamine compound to ensure that the polyamine compound, once reacted, will have a free unreacted primary amine site available for reaction with the monoglycidyl capping agent. Once the amine reaction onto the substituted aromatic glycidyl ester composition is complete, the excess amine, if any, should be vacuum distilled off, typically at 20 in.Hg to 30 in.Hg for 30 to 480 minutes.

Suitable polyamines are those which have at least two primary amine groups, where one of the primary amine groups is used for reaction with the carboxyl group on phenolic compound. A non-limiting example of polyamines useful in the practice of the invention is represented by the formula:



(XXVI)

wherein n is an average of integers between about 0 and 10, preferably between 1 and 4; and X is a divalent branched or unbranched hydrocarbon radical having about 1-18 carbons, one or more aryl or alkaryl groups, or one or more alicyclic groups. Preferably, X is a lower alkylene radical having 1-10, preferably 2-6, carbon atoms. Such alkylene polyamines include methylene polyamines, ethylene polyamines, butylene polyamines, propylene polyamines, pentylene polyamines, hexylene polyamines, heptylene polyamines, etc. The higher homologs of such amines and related aminoalkyl-substituted piperazines are also included. Specific examples of polyamines include ethylene diamine, triethylene tetramine, tris(2-aminoethyl)-amine, 1,2-

and 1,3-propylene diamine, trimethylene diamine, 1,2- and 1,4-butanediamine, hexamethylene diamine, decamethylene diamine, octamethylene diamine, diethylene triamine, triethylene tetramine, di(heptamethylene)triamine, tripropylene tetramine, tetraethylene pentamine, trimethylene diamine, pentaethylene hexamine, di(trimethylene)triamine, p- and m-xylylene diamine, methylene dianiline, 2,4-toluenediamine, 2,6-toluenediamine, diaminodiphenylmethane, polymethylene polyphenylpolyamine, diaminocyclohexane, isophoronediamine, 1,3-bis(aminomethyl)cyclohexane, 4,4'diaminodicyclohexylmethane, and mixtures thereof. Higher homologs, obtained by condensing two or more of the above-illustrated alkylene amines, are also useful. More preferred are those polyamines containing at least one secondary amino group in addition to the at least two primary amino groups, and multiple divalent hydrocarbon radicals having 2-8 and preferably from 2-4 carbon atoms. Examples of the preferred polyamines are ethylenediamine, diethylenetriamine, triethylenetetramine, and tetraethylenepentamine.

The ethylene type polyamines, examples of which are mentioned above, are especially useful for reasons of cost and effectiveness. Such polyamines are described in detail under the heading "Diamines and Higher Amines" in Kirk-Othmer, Encyclopedia of Chemical Technology, Second Edition, Vol. 7, pp. 22-39. They are prepared most conveniently by the reaction of an alkylene chloride with ammonia or by reaction of an ethylene imine with a ring-opening reagent such as ammonia. These reactions result in the production of the somewhat complex mixtures of alkylene polyamines, including cyclic condensation products such as piperazines. These

mixtures are satisfactory in preparing the compositions of this invention.

Hydroxy polyamines, e.g., alkylene polyamines having one or more hydroxyalkyl substituents on the nitrogen atoms, are also useful in preparing amides of this invention. Preferred hydroxyalkyl-substituted alkylene polyamines are those in which the hydroxyalkyl group has less than about 10 carbon atoms. Examples of such hydroxyalkyl-substituted polyamines include N-(2-hydroxyethyl)-ethylene diamine, N,N'-bis(2-hydroxyethyl)ethylene diamine, monohydroxypropyl-substituted diethylene triamine, dihydroxypropyltetraethylene pentamine and N-(3-hydroxybutyl)tetramethylene diamine. Higher homologs obtained by condensation of the above-illustrated hydroxyalkyl-substituted alkylene amines through amino radicals or through hydroxy radicals are likewise useful.

The c) reactive surfactant useful in the invention is one which contains a functional moiety reactive with secondary amines and a hydrophilic moiety of a nature and length effective to disperse the curing agent in water. The surfactant composition has a hydrophilic moiety of a nature and length effective to disperse the curing agent in water using only 1 wt% to 10 wt%, preferably 2 wt% to 6 wt%, more preferably only 2 wt% to 4 wt% of the surfactant composition, based on the weight of curing agent solids, to stably disperse the solids in the water borne curing agent composition at a solids level preferably from 45 wt% or more, more preferably 50 wt% or more, and most preferably 60 wt% or more. While one may use more surfactant composition than 10 wt%, or make an aqueous dispersion of less than 45 wt% solids, the surfactants employed to disperse the

curing agent of the invention have the ability to stably disperse at least45 wt% solids at surfactant composition levels of 2 to 6 wt% without any noticeable phase separation to the naked eye at 30 days of still storage.

The average particle size in the aqueous dispersions of the invention are also quite small, on the order of less than 2 μ, preferably 0.5 μ or less. It is desirable to have as low a particle size as possible at as high a solids level as possible to obtain improved coalescence, thereby obtaining optimum film mechanical properties.

The reactive surfactant molecule contains groups reactive with a secondary amine group. By a group reactive with secondary amine group is not meant that the reactive surfactant molecule must be reacted onto a secondary amine group, but only that the functional group on the reactive surfactant molecule have sufficient reactivity to react with a secondary amine group. However, included within the reactive surfactant molecules used in the invention are those which have been altered such as by way of pre-reacting the reactive surfactant molecule with a polyamine compound.

Suitable reactive groups on the reactive surfactant molecule include epoxide, carboxylic acid and anhydrides thereof, and isocyanate functionalities. Any number of the same or independently different types of functional groups reactive with secondary amines may be bonded to the surfactant molecule. For example, the surfactant molecule may contain 1, 2, 3, etc. epoxide and/or carboxylic acid groups per surfactant molecule. Suitable hydrophilic moieties in the surfactant

molecule include, but are not limited to, polyoxyalkylene monool or polyol residues.

According to the more preferred embodiments, n and p in formulae I, II or III represent the number of repeating units of oxyalkylene groups effective to stably disperse the curing agent in water, which can range from 0 to 4000, preferably from 50 to 1000, provided that n+p= is at least 15; and w represents the number of epoxy glycidyl ether units, ranging from 0 to 20, preferably from 0 to 5. The surfactant preferably has a number average molecular weight within the range of from 1000, preferably from 2000, to 105,000, preferably to 50,000, more typically to 20,000. Generally, the quoted number of units is the whole number closest to the statistical average, and the peak of the distribution. Positive real numbers as used herein refer to a number which is positive and includes integers and fractions of integers. In the above formulas I-III, the depicted sequence of groups is not intended to represent an order or a block structure. The above formulas I-III are to be broadly read as representing random structures, block structures, or random-block structures. Further, the n units broadly represent a homo or block or random selection. For example, the n units may represent n repeating units of oxyethylene groups, a random mixture of oxyethylene and oxypropylene groups, or blocks of oxyethylene and oxypropylene groups in any sequence.

With respect to formulas I-III above, each of the surfactant molecules contain a polyoxyalkylene moiety. With respect to formula I above, the hydrophilic carboxylic acid can be produced through the oxidation of a polyoxyalkylene molecule by any conventional known

process, including, but limited to, the processes described in U.S. Patent No. 5,250,727. The molecule corresponding to formula II above may be prepared by reacting the hydrophilic carboxylic acid with an epoxy resin, or by reacting the carboxylic acid with an epihalohydrin, followed by dehydrohalogentation, in which case w is 0. The molecule corresponding to formula III above may be prepared by reacting a polyoxyalkene monool or polyol with an epoxy resin, or by reacting it with an epihalohydrin followed by dehydrohalogentation, in which case w is 0. As each of these surfactant molecules corresponding to formulas I-III contain polyoxyalkylene moieties, the preparation of polyoxyalkene monools and polyols is now described.

Generally, the quoted number of units is the whole number closest to the statistical average, and the peak of the distribution. In a more usual embodiment according to formula I, the n units represent oxythylene or oxyethylene and oxypropylene groups, p is 0, and m is one or two, the number average molecular weight being from at least 1000 to 20,000.

The hydrophilic polyoxyalkyene molecule may be prepared by reacting an intiator molecule with an alkylene oxide under oxyalkylation conditions well known to those of ordinary skill in the art of polyether polyols, such as, for example, the process disclosed by Wurtz in 1859 and Encyclopedia of Chemical Technology, Vol. 7, pp. 257-262, published by Interscience Publishers, Inc. (1951) or in U.S. Pat. No. 1,922,459.

Any suitable alkylene oxide may be used such as ethylene oxide, propylene oxide, butylene oxide, amylene oxide, and mixtures of these oxides. The polyoxyalkylene

monools and polyols may be prepared from other starting materials such as tetrahydrofuran and alkylene oxide-tetrahydrofuran mixtures; epihalohydrins such as epichlorohydrin; as well as aralkylene oxides such as styrene oxide. The particular individual or combination of alkylene oxides chosen must be effective to stably disperse the particular species of curing agent in water.

The alkylene oxides may be added to the initiator, individually, sequentially one after the other to form blocks, in mixture to form a heteric polyether, or blocks of mixed oxyalkylene and homogeneous oxyalkyene groups. Suitable homo polyoxyalkylene monools and polyols include polyoxyethylene monool or polyol, and polytetramethylene monool or polyol. Suitable block copolymers include, for example, blocks of polyoxypropylene and polyoxyethylene, poly-1,2-oxybutylene and polyoxyethylene, poly-1,4-tetramethylene and polyoxyethylene. The blocks of polyoxypropylene or polyoxybutylene are preferably internal relative to the outermost block of other poloxyalkylenes. Other copolymers include the heteric copolymer monools and polyols prepared from blends, optionally with sequential addition, of two or more alkylene oxides. The polyalkylene polyether polyols may be terminated with either primary or secondary hydroxy groups. We have found that polyoxyalkylene molecules containing ethylene oxide work well, such as those having an EO/PO/EO block structure. Thus, where propylene or butylene oxide is used, it is preferred that the amount of such oxides is no more than 40 mole percent to ensure that the polyoxyalkylene molecule overall is hydrophilic.

The intiator molecule can be monofunctional or polyfunctional. The functionality of the surfactant will nominally be that of the intiator. The actual functionality of the surfactant molecule will be somewhat less due to the formation of chain terminating points of unsaturation during the oxyalkylation process, especially where propylene oxide is added in significant quantities.

Examples of the initiator molecule include the alkanols and low molecular weight polyols having a number average molecular weight of 500 or less, such as alkanols having an average number of carbons ranging from 1 to 32, like methanol, ethanol, propanol, butanol, and the NEODOL alcohols commercially available from Shell Chemical Company (NEODOL is a trademark), or ethylene glycol, propylene glycol, dipropylene glycol, trimethylene glycol, 1,2-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, hydroquinone, resorcinol glycerol, glycerine, 1,1,1-trimethylolpropane, 1,1,1-trimethylolethane, pentaerythritol, 1,2,6-hexanetriol, alpha -methyl glucoside, sucrose, sorbitol, and compounds derived from phenol such as 2,2-bis(4-hydroxyphenyl)-propane, commonly known as Bisphenol A. Preferable initiator molecules include alkanols having an average number of carbons ranging from 1 to 20, trimethylolpropane, ethylene and propylene glycol, glycerine, dipropylene glycol, and 2,2-bis(4-hydroxyphenyl)-propane and blends thereof.

Other initiators include aromatic amines such as aniline, N-alkylphenylene-diamines, 2,4'-, 2,2'-, and 4,4'-methylenedianiline, 2,6- or 2,4-toluenediamine, vicinal toluenediamines, o-chloro-aniline, p-amino-aniline, 1,5-diaminonaphthalene, methylene dianiline,

the various condensation products of aniline and formaldehyde, and the isomeric diaminotoluenes; and aliphatic amines such as mono-, di, and trialkanol-amines, ethylene diamine, propylene diamine, diethylene-triamine, methylamine, triisopropanolamine, 1,3-diamino-propane, 1,3-diaminobutane, and 1,4-diaminobutane.

Other initiator molecules include polyhydric polythioethers, polyhydroxyl-containing phosphorus compounds, polyacetals, and aliphatic thiols.

Once the polyoxyalkylene monool or polyol is made, the molecule may be oxidized as described above to produce a surfactant represented by formula I, and further reacted with an epoxy resin to produce a surfactant corresponding to formula II, or the monool or polyol may be reacted with an epoxy resin to prepare a surfactant molecule corresponding to formula III.

As noted above, the hydrophilic carboxylic acid can be produced by oxidation of a polyoxyalkylene molecule by any conventional know process, including, but limited to, the processes described in U.S. Patent No. 5,250,727. Generally, oxygen is added to the polyalkylene glycol in the presence of a free radical (e.g., 2,2,6,6-tetramethyl-1-piperidinyloxy) and an inorganic acid (e.g., nitric acid) to produce the carboxylic acid until substantially all of the alcohol groups are oxidized to carboxylic acid groups.

The epoxy-functionality can be introduced by reacting a polyether monool or polyol, or its carboxylic acid derivative, with an epoxy resin having a functionality of at least 1.5 epoxide group per molecule under conditions effective to react the hydroxyl or acid group on the polyoxyalkylene molecule with the epoxide group. Typically, the mole ratio of the monool, polyol,

or carboxylic acid to epoxy resin is within the range of 1:1 to 1:500. If desired, the monool or polyol may be reacted with a stoichiometric excess of the epoxy resin such that the surfactant composition contains free unreacted epoxy resin molecules. The reaction is typically carried out at a temperature from ambient temperature to an elevated temperature sufficient to react the hydroxyl or acid group and the epoxide group preferably within the range of from 90 °C to 150 °C for a time effective to produce the reaction products. The progress of the reaction can be monitored and targeted to produce the desired product by measuring the hydroxyl number, acid equivalent weight and/or the epoxy equivalent weight of the reactant mixture. Generally, the reaction mixture is heated until 95%, preferably until at least 99%, of the original number of equivalents of hydroxyl or acid equivalents is consumed. The reaction can proceed at atmospheric pressure.

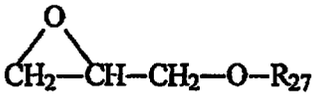
Preferably, the reaction between the hydroxyl or carboxylic acid groups, and the epoxide groups, in the course of making the surfactant molecule, is carried out in the presence of a catalyst. The catalysts are bases or metal chelates such as, for example, ammonium compounds, phosphonium compounds, tertiary amines, and phosphines. Examples of more preferred catalysts include, for example, triphenylphosphonium acid acetate, ethyltriphenyl phosphonium iodide, benzyldimethylamine, triphenylphosphine, tributylamine, aluminium salicylates, tetramethylammonium hydroxide and the like. The amount of catalyst present is preferably from 0.05 to 2.0 weight percent based on the total weight of the epoxy resin and the polyoxyalkylene molecule.

The epoxy resins used to make the reactive surfactant can be any reactive epoxy resin having a 1,2-epoxy equivalency (functionality) preferably, on the average, greater than 1.5 epoxide groups per molecule. Any of those described above with respect to making the substituted glycidyl ester compound are suitable for making a reactive surfactant compound.

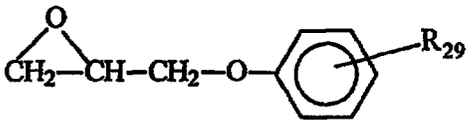
The optional d) monoglycidyl, monocarboxylic acid, or monoisocyanate capping agent can be an aliphatic, alicyclic, or aromatic compound attached to the functional group. At least with respect to making the curing agent composition, reacting at least a portion of unreacted primary amine hydrogen with the capping agent reduces the chance for carbamate formation from atmospheric moisture reacting with the primary amine hydrogens, normally appearing as a blush on the coating and leading to chain scission. In addition to reducing the effect of blushing by reacting out with the capping agent some or all of the primary amine groups in the curing agent composition, or in the surfactant composition, if any exist, the molecule will have a free secondary amine hydrogen active for reaction with epoxy groups. In a preferred embodiment, it is desirable to avoid reacting the capping agent with functional groups which would yield the structure -NH-CO-, since the carboxy group tends to deactivate the amine hydrogen. Reacting a primary amine on the a substituted glycidyl ester-amine adduct with a glycidyl functionality, however, leaves the secondary amine hydrogen more active for reaction with an epoxy resin. Thus, one can achieve the dual advantage of reducing blush while retaining sufficient reactivity to cure the system at ambient temperatures in the absence of external catalysts.

Reaction with a monoglycidyl capping agent also leads to the formation of a hydroxyl group, which would also be available to react with the epoxy component. In view of their ready availability, good chemical resistance, hydrolytic stability, and provision of a reactive secondary amine hydrogen and an epoxide reactive site, the monoglycidyl capping agents are preferred.

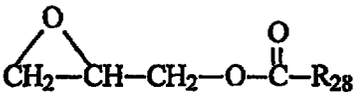
Non-limiting examples of monoglycidyl capping agents which are suitable for use in the invention include:



(XXVII)



(XXVIII)



(XXIX)

wherein R_{27} and R_{28} are the same or different and are a branched or linear alkyl, an alkalicyclic, polyoxyalkyl, or alkenyl group having 2-100 carbon atoms, optionally branched,; and R_{29} is hydrogen or a branched or unbranched alkyl having 1-18 carbon atoms. There may be more than one type of R_{29} group attached to the aromatic ring.

These categories would include the unsaturated epoxy hydrocarbons of butylene, cyclohexene, styrene oxide and the like; epoxy ethers of monovalent alcohols such as methyl, ethyl, butyl, 2-ethylhexyl, dodecyl alcohol and others; epoxides of the alkylene oxide adducts of alcohols having at least 8 carbon atoms by the sequential addition of alkylene oxide to the corresponding alkanol (ROH), such as those marketed

under the NEODOL name; epoxy ethers of monovalent phenols such as phenol, cresol, and other phenols substituted in the o- or p- positions with C_1-C_{21} branched or unbranched alkyl. aralkyl, alkaryl, or alkoxy groups such as nonylphenol; glycidyl esters of mono-carboxylic acids such as the glycidyl ester of caprylic acid, the glycidyl ester of capric acid, the glycidyl ester of lauric acid, the glycidyl ester of stearic acid, the glycidyl ester of arachidic acid and the glycidyl esters of alpha, alpha-dialkyl mono-carboxylic acids described in U.S. Pat. No. 3,178,454, epoxy esters of unsaturated alcohols or unsaturated carboxylic acids such as the glycidyl ester of neodecanoic acid, epoxidized methyl oleate, epoxidized n-butyl oleate, epoxidized methyl palmitoleate, epoxidized ethyl linoleate and the like; phenyl glycidyl ether; allyl glycidyl ethers, and acetals of glycidaldehyde.

Specific examples of monoglycidyl capping agents useful to the practice of the invention include alkyl glycidyl ethers with 1-18 linear carbon atoms in the alkyl chain such as butyl glycidyl ether or a mixture of C_8-C_{14} alkyls, cresyl glycidyl ether, phenyl glycidyl ether, nonylphenylglycidyl ether, p-tert-butylphenyl glycidyl ether, 2-ethylhexyl glycidyl ether, and the glycidyl ester of neodecanoic acid.

The aliphatic based capping agents are usually hydrophobic in character, which tends to improve the coalescence properties of the epoxy-curing agent mixture at low temperatures, and tends to lower the glass transition temperature of the film or coating. The lower glass transition temperature improves the impact strength of the cured film. Aromatic based monoglycidyl capping agents, however, have the advantage of rendering

the cured film more rigid, chemically resistant, and resistant to stresses at high temperatures. Any one of these types of capping agents may be used, and mixtures thereof are also advantageous to attain an overall balance of mechanical strength and chemical resistance.

If used in the manufacture of the surfactant composition for the group of embodiments I, and in the manufacture of the curing agent composition, the capping agent is reacted with the substituted glycidyl ester-amine adduct in an amount effective to provide a water borne curing agent composition which is compatible with neat or water borne bisphenol A and bisphenol F type liquid diglycidyl ether epoxy resins as well as epoxidized phenolic novolac resins. Usually, the monoglycidyl capping agent is reacted with the substituted glycidyl ester-amine adduct at a molar ratio of 0.5:1 to 2:1. While one may use more than a 2:1 ratio, it is not necessary to do so in order to convert the primary amine groups into secondary amine groups and reduce the blushing effect. If desired, the surfactant composition, if needed, and water borne curing agent composition can be partially capped with the monoglycidyl capping agent, because even a partial capping will have some effect on blush reduction.

In a preferred embodiment of the surfactants according to formula V and VI, R_1 is greater than 12; c is an integer from 1-4; k is an integer from 0-4. For ease of manufacture, the latter structure is preferred. However, where a capping agent is used, R_3 is the residue of an alkyl glycidyl ether having 1-24 branched or unbranched carbon atoms in the alkyl chain, an alkaryl glycidyl ether, an aryl glycidyl ether, an allyl glycidyl ether, an alicyclic alkyl glycidyl

ether, or a glycidyl ester of a monocarboxylic acid. In a more preferable embodiment, R_3 is the residue of an alkyl glycidyl ether having 2-18 carbon atoms or an alkaryl glycidyl ether wherein the alkyl has 1-24 carbon atoms, and most preferably is the residue of butyl glycidyl ether, cresyl glycidyl ether, phenyl glycidyl ether, nonylphenyl glycidyl ether, p-tert-butyl glycidyl ether, or an alkyl glycidyl ether having 8-16 branched or unbranched alkyl carbon atoms.

The surfactant composition can be made and isolated as such, or it can be made "in-situ." There are several methods for making the surfactant composition in situ as described above. The amount of reacted surfactant compound in the curing agent composition, as noted above, can range from only 1 wt% to 10 wt%. The surfactant composition be combined with the curing agent composition by admixing the surfactant composition with the curing agent composition in an amount calculated to provide 1 wt% to 10 wt% of reacted surfactant compound based on the weight of the curing agent and the surfactant composition, or preferably, the reacted surfactant compound can be combined with the curing agent composition by reacting the reactive surfactant in situ in a stoichiometric excess of the curing agent composition, at any stage of making the curing agent composition beyond the manufacture of the substituted glycidyl ester compound, to obtain a curing agent composition containing from 1 to 10 wt% of the reacted surfactant compound. In the latter embodiment, the curing agent composition contain the same substituted glycidyl ester moiety as does the surfactant composition. In either case, the curing agent composition of the invention can then be mixed with

water in amounts necessary to produce the desired level of solids. Thus, the water borne curing agent of the invention advantageously contains a reacted surfactant having a moiety which is identical in structure to the curing agent it is designed to disperse in water, and also contains a moiety which is a high molecular weight hydrophilic strand adapted for stably dispersing the curing agent in water hydrophilic strand adapted for stably dispersing the curing agent in water.

Within the group of embodiments B it is preferred, as to the order of reaction to first make the amido-polyamine compound followed by reaction with the monoglycidyl capping agent, or if desired, a mixture of the monoglycidyl capping agent and the reactive surfactant compound, to ensure that the polyamine compounds react onto the carboxylic acid functionalities on the phenolic compounds. Reacting all ingredients together in situ would result in competing reactions where monoglycidyl functionalities undesirably react with the acid groups on the phenolic compound or with both primary amine functionalities on the polyamine compound, thereby effectively reducing the number of species having amidopolyamine linkages between the phenolic compound and the polyamine compound, end capped with the monoglycidyl capping agent. Thus, it is preferred to make, in a first step, at least a portion of the substituted aryl amidopolyamine compound, followed by reaction(s) with the capping agent or a mixture of the capping agent and the reactive surfactant. It is more preferred to react all of the substituted phenolic compound with all of the polyamine compound at the desired molar ratio to form the substituted aryl amidopolyamine compound, sequentially followed by

reacting onto the substituted aryl amidopolyamine compound the remainder of the reactants necessary to make the surfactant composition or the water borne curing agent composition.

The reactive surfactant useful in the invention is one which contains a functional moiety reactive with secondary amines and a hydrophilic moiety of a nature and length effective to disperse the curing agent in water. The reaction product of the surfactant with the end capped substituted aryl amidopolyamine, along with other unreacted species or by-products, is what is identified herein as the reacted surfactant compound. The reacted surfactant has a hydrophilic moiety of a nature and length effective to disperse the curing agent in water using only 1 wt% to 10 wt%, preferably 2 wt% to 6 wt%, more preferably only 2 wt% to 4 wt% of the surfactant composition, based on the weight of curing agent solids, to stably disperse the solids in the water borne curing agent composition at a solids level preferably from 45 wt% or more, more preferably 50 wt% or more, and most preferably 60 wt% or more. While one may use more reacted surfactant than 10 wt%, or make an aqueous dispersion of less than 45 wt% solids, the reacted surfactants employed to disperse the curing agent of the invention have the ability to stably disperse at least 45 wt% solids at reacted surfactant compound levels of 2 to 6 wt% without any noticeable phase separation to the naked eye after at least 3 days of still storage.

The average particle size in the aqueous dispersions of the invention are also quite small, on the order of less than 1 μ, preferably 0.5 μ or less, more preferably 0.35 μ or less. It is desirable to have as

low a particle size as possible at as high a solids level as possible to obtain improved coalescence, thereby obtaining optimum film mechanical properties.

The surfactant composition of group of embodiments B, comprises a reacted surfactant compound represented by one or more of the formulas IX and X wherein R_1 preferably is a branched or unbranched, substituted or unsubstituted, monovalent hydrocarbyl group having more than 12, more preferably 14 or more; R_2 and R_4 each independently represent a branched or unbranched, substituted or unsubstituted, divalent hydrocarbyl group preferably having 2-6 carbon atoms, or groups of formula (VII) or (VIII) wherein R_6 represents a branched or unbranched, substituted or unsubstituted, divalent hydrocarbyl group having 2-24 carbon atoms; R_{13} is a branched or unbranched, substituted or unsubstituted, monovalent hydrocarbyl having 1-24 carbon atoms, an aryl group, an alkaryl group, or an aralkyl group; c represents preferably an integer from 1-10; and Surf represents the c) reactive surfactant residue; provided that when c=0, the -CO-Surf group and the -CH_2-CHOH-CH_2-O-Surf group are bonded to the nitrogen atom farthest from the depicted amide group. In a more preferred embodiment, R_{13} is the residue of an alkyl glycidyl ether having 1-24 branched or unbranched carbon atoms in the alkyl chain, an alkaryl glycidyl ether, an aryl glycidyl ether, an allyl glycidyl ether, an alicyclic alkyl glycidyl ether, or a glycidyl ester of a monocarboxylic acid. In a most preferred embodiment, R_{13} is the residue of an alkyl glycidyl ether having 2-18 carbon atoms or an alkaryl glycidyl ether wherein the alkyl has 1-24 carbon atoms, and most

preferably is the residue of butyl glycidyl ether, cresyl glycidyl ether, phenyl glycidyl ether, nonylphenyl glycidyl ether, p-tert-butyl glycidyl ether, or an alkyl glycidyl ether having 8-16 branched or unbranched alkyl carbon atoms.

The reactive surfactant molecule contains groups reactive with the secondary amine group on the substituted aryl amidoamine molecule. Suitable reactive groups on the surfactant molecule include epoxide, carboxylic acid and anhydrides thereof, and isocyanate functionalities. Any number of the same or independently different types of functional groups reactive with secondary amines may be bonded to the surfactant molecule. For example, the surfactant molecule may contain 1, 2, 3, etc. epoxide and/or carboxylic acid groups per surfactant molecule. Suitable hydrophilic moieties in the surfactant molecule include, but are not limited to, polyoxyalkylene monool or polyol residues.

For the group of embodiments A of the surfactant compositions the curing agent composition used is advantageously the reaction product of the a) phenolic compound, the e) polyepoxide compound, the b) polyamine compound, and the d) capping agent, as described above with respect to the surfactant composition, and more preferably, contains all the same reactants as used to make the surfactant composition.

For the group of embodiments B of the surfactant compositions, the curing agent composition used is advantageously the reaction product of a substituted aryl amidopolyamine compound with the capping agent and more preferably, contains all the same reactants as used

to make the end-capped substituted aryl amidopolyamine compound for use in the surfactant composition.

In general, the curing agents of the invention can optionally be mixed with other conventional curing agents. The amount of other conventional curing agents admixed will depend upon the requirements placed upon the end product and the efficiencies one desires to achieve. If the end use does not require a product which has high end physical properties and/or it is not important to have lowered processing times, then greater amounts of an inexpensive conventional curing agent can be mixed with the curing agent composition of the invention. The amount of the curing agent in the water borne curing agent composition can range in the low end of from 1 to 50 wt% based on the weight of all curing agents, but is preferably from 50 wt% to 100 wt%.

Conventional curing agents are usually polyamines with at least 2 nitrogen atoms per molecule and at least two reactive amine hydrogen atoms per molecule. The nitrogen atoms are linked by divalent hydrocarbyl groups. Other hydrocarbyl groups such as aliphatic, cycloaliphatic or aromatic groups may also be singly linked to some of the nitrogen atoms. These polyamines contain at least 2 carbon atoms per molecule. Preferably polyamines contain about 2 to 6 amine nitrogen atoms per molecule, 2 to 8 amine hydrogen atoms per molecule, and 2 to 50 carbon atoms.

Examples of the polyamines useful as conventional curing agents for epoxy resins include aliphatic polyamines such as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, dipropylene triamine, tributylene tetramine, hexamethylene diamine, dihexa-

methylene triamine, 1,2-propane diamine, 1,3-propane diamine, 1,2-butane diamine, 1,3-butane diamine, 1,4-butane diamine, 1,5-pentane diamine, 1,6-hexane diamine, 2-methyl-1,5-pentanediamine, 2,5-dimethyl-2,5-hexanediamine and the like; cycloaliphatic polyamines such as isophoronediamine, 4,4'-diaminodicyclohexylmethane, methane diamine, 1,2-diaminocyclohexane, 1,4-diaminocyclohexane, and diamines derived from "dimer acids" (dimerized fatty acids) which are produced by condensing the dimer acids with ammonia and then dehydrating and hydrogenating; adducts of amines with epoxy resins such as an adduct of isophoronediamine with a diglycidyl ether of a dihydric phenol, or corresponding adducts with ethylenediamine or m-xylylenediamine; araliphatic polyamines such as 1,3-bis(aminomethyl)benzene; aromatic polyamines such as 4,4'-methylenedianiline, 1,3- phenylenediamine and 3,5-diethyl-2,4-toluenediamine; amidoamines such as condensates of fatty acids with diethylenetriamine, triethylenetetramine, etc.; and polyamides such as condensates of dimer acids with diethylenetriamine, triethylenetetramine, etc. Some commercial examples of polyamines include EPI-CURE Curing Agent 3140 (a dimer acid-aliphatic polyamine adduct), EPI-CURE Curing Agent 3270 (a modified aliphatic polyamine), EPI-CURE Curing Agent 3274 (a modified aliphatic polyamine), EPI-CURE Curing Agent 3295 (an aliphatic amine adduct), EPI-CURE Curing Agent 3282 (an aliphatic amine adduct), EPI-CURE Curing Agent 3055 (an amidopolyamine), EPI-CURE Curing Agent 3046 (an amidopolyamine) and EPI-CURE Curing Agent 3072 (modified amidoamine), and EPI-CURE Curing Agent 3483 (an aromatic polyamine) (EPI-CURE is a trademark). Mixtures of polyamines can also be used.

The epoxy resin component for reaction with the water borne curing agent composition has at least one 1,2-epoxy group per molecule. Mixtures of epoxy compounds having one epoxy functionality and two or more epoxy groups are also suitable. The epoxy compounds having two or more epoxy groups per molecule means that the nominal functionality is two or more. Generally epoxy resins contain a distribution of compounds with a varying number of 1,2-epoxy equivalency. The actual average functionality of these epoxy compounds is 1.5 or more. Any of the epoxy compounds mentioned above with respect to the epoxy resin used for reacting onto the polyoxyalkylene monool, polyol, or carboxylic acid can be employed as the epoxy resin component for reaction with the water borne curing agent.

Commercial examples of the preferred epoxy compounds having a nominal functionality of two or more include, for example, EPON Resins DPL-862, 828, 826, 825, 1001, EPONEX Resin 1510, HELOXY Modifiers 107, 67, 68, and 32; all available from Shell Chemical Company and Union Carbide Epoxy Resins ERL-4221, -4289, -4299, -4234 and -4206 (EPON, EPONEX and HELOXY are trademarks).

The curing agent composition of the invention may include other additives, such as fillers, elastomers, stabilizers, extenders, plasticizers, accelerators, pigments, reinforcing agents, flow control agents and flame retardants depending on the application.

Advantageously, the curable epoxy resin composition is cured in the absence of catalyst compounds which accelerate the reaction between the curing agent and the epoxy resin, commonly known as accelerators. An accelerator, however, can be included, if desired, to

increase the cure rate of the epoxy resin-curing agent system beyond that already achieved in its absence. Various amine-compatible accelerators can be used as long as they are soluble in the amine curing agents. Examples of accelerators include metal salts such as, for example, sulfonates, phosphonates, sulphates, tetrafluoroborates, carboxylates and nitrates of Groups IA, IIA and transition metal series of the Periodic Table (CAS version), preferably Mg, Ca, Zn and Sn salts, and complexes thereof; inorganic acids such as, for example, HBF_4, H_2SO_4, $H2NSO_3H$ and H_3PO_4; carboxylic acids, preferably hydroxy-substituted carboxylic acids such as, for example, salicylic, lactic, glycolic and resorcylic; phenolic compounds such as, for example, phenol, t-butylphenol, nonylphenol and bisphenol A; imidazoles; cyanamide compounds such as dicyandiamide and cyanamide; sulphonamides such as, for example p-toluenesulphonamide, methanesulphonamide, N-methylbenzenesulphonamide and sulfamide; and imides such as, for example, phthalimide, succinimide, perylenetetracarboxylic diimide and saccharin.

When the cure rate at the desired temperature is suboptimal, it is sometimes desirable to include the accelerator. For example, for adhesive applications and civil engineering applications where application at low temperature is desired, it may be desirable to include the accelerator. The accelerators are typically present in an amount of from 0.1 weight percent to 10 weight percent, preferably to 5 weight percent, based on the epoxy resin, if used at all.

For coating applications, the curable epoxy resin component, or the water borne curing agent composition, can also contain pigments of the conventional type such

as iron oxides, lead oxides, strontium chromate, carbon black, titanium dioxide, talc, barium sulphate, phthalocyanine blue and green, cadmium red, iron blue, chromic green, lead silicate, silica, silicates and the like. Such pigments can be added to the polyamine curing agent component or the epoxy resin component prior to mixing them together. Their amounts usually range from 20 to 100 pbw based on the weight of the epoxy resin and the curing agent composition.

For floor topping application, the curable epoxy resin component or the water borne curing agent composition can also contain a filler such as sand, other siliceous materials, iron or other metals. Small amounts of thixotropic agents, colouring agents, inert plasticizers, and levelling agents can also be incorporated in the curable epoxy resin composition if desired. These curable flooring compositions can be trowelled, sprayed or brushed on to a floor substrate.

Re-inforcing agents may be added to either of the components, and include natural and synthetic fibres in the form of woven, mat, monofilament, chopped fibres and the like. Other materials for re-inforcing include glass, ceramics, nylon, rayon, cotton, aramid, graphite and combinations thereof. Suitable fillers include inorganic oxides, inorganic carbonates, ceramic microspheres, plastic microspheres, glass microspheres, clays, sand, gravel and combinations thereof. The fillers can be used in amounts suitably from 0 to 100 pbw of the combined epoxy/curing agent components.

Aside from coating applications, the curing agent compositions of the invention and the two component compositions utilizing the curing agents compositions can be used in such applications as flooring, casting,

crack or defect repair, moulding, adhesives, potting, filament winding, encapsulation, structural and electrical laminates, composites and the like.

The two component compositions of the invention are mixed and cured, preferably in the absence of external accelerators, in a wide range of temperatures ranging from -25 °C to 100 °C.

The curing agent compositions of the invention can also be used in thermosetting powder coating compositions prepared by the various methods known to the powder coating industry: dry blending, melt compounding by two roll mill or extruder and spray drying. Typically the process used is the melt compounding process: dry blending solid ingredients in a planetary mixer and then melt blending the admixture in an extruder at a temperature within the range of 80 °C to 130 °C. The extrudate is then cooled and pulverized into a particulate blend.

The thermosetting powder composition can then be applied directly to a substrate of ,e.g., a metal such as steel or aluminum. Non-metallic substrates such as plastics and composites can also be used. Application can be by electrostatic spraying or by use of a fluidized bed. Electrostatic spraying is the preferred method. The coating powder can be applied in a single sweep or in several passes to provide a film thickness after cure of 2.0 to 15.0 mils.

The substrate can optionally be preheated prior to application of a powder composition to promote uniform and thicker powder deposition. After application of the powder, the powder-coated substrate is baked, typically at 120 °C, preferably from 150 °C, to 205 °C for a time sufficient to cure the powder coating composition,

typically from 1 minute to 60 minutes, preferably from 10 minutes to 30 minutes.

The following examples illustrate an embodiment of the invention and are not intended to limit the scope of the invention.

EXAMPLES

In the examples 1 and 2 the following reagents are used:

DIAMINE

is a 2 methyl-pentamethylene diamine commercially available as DYTEK-A having a molecular weight of about 119 (DYTEK is a trademark).

HELOXY Modifier 62

is a commercial grade of ortho-cresyl glycidyl ether manufactured by Shell Chemical Company, that is produced by treatment of ortho-cresol with epichlorohydrin and sodium hydroxide. HELOXY Modifier is a thin liquid having a viscosity at 25 °C of 7 centipoise and an epoxide equivalent weight of 175 to 195.

SURFACTANT COMPOSITION A

is a carboxylated poloxyethylene molecule derived from carboxylating a polyoxyethylene monool having a number average molecular weight of 5000.

EPOXY RESIN A

is a dispersion of an epoxy resin substantially equivalent to EPON 1001 resin having an equivalent weight per epoxide group of 450-550, in water having a functionality of less than 2.

Example 1

This example illustrates the synthesis of self emulsifiable water borne curing agent composition containing a surfactant composition made in situ. The

curing agent is a substituted aromatic glycidated ester-amine adduct end capped with a monoglycidyl ether, stabilized as an oil in water emulsion through a reacted surfactant made in situ by reacting Surfactant A onto a substituted aromatic glycidated ester-amine adduct. In Stage 1, the substituted aromatic glycidated ester compound is made. In Stage 2, the remainder of the reactions are described.

Stage 1

500 grams of EPIKOTE 828 in xylene, which is a bisphenol A based diepoxy resin available from Shell Chemicals Europe (EPIKOTE is a trademark); 327 grams of a 63 wt% 3-alkyl substituted salicyclic acid mixture in xylene (corresponding to about 20 mole% per epoxy group), in which the alkyl group contains from 14 to 18 carbon atoms and the mixture contains less than 15 mole% of C_{14}-C_{18} alkyl phenols and less than 5 mole% of dicarboxylic acid species; and 0.15 grams of ethyltri-penylphosphonium iodide were mixed together in a vessel equipped with a condenser. The reaction temperature was increased to 175 °C (heating up to 110 ° C in 30 minutes, holding for another 30 minutes at 110 °C and then heating to 175 °C within the next 60 minutes), and holding the temperature at 175 °C for the next 30 minutes, for a total reaction time of 2.5 hours. Water and xylene were stripped off. Subsequently, the substituted aromatic glycidyl ester composition was allowed to cool. Once cooled, the product was dissolved in xylene to about 80 wt% solids. The product had an acid number of zero (theoretical) in solution and an acid number of zero (theoretical) based on solids. This product is designated as SSAEP.

Stage 2

A 4 necked 2 litre round-bottomed glass flask was equipped with a condenser having a water trap, a nitrogen inlet, an acid inlet, and the DIAMINE inlet. The flask was flushed with nitrogen. 357 g of the DIAMINE, representing about 6 equivalents, were charged and heated to 93 °C. 505 g of SSAEP, representing about 1 equivalent, were charged to the flask at a rate such that the heat of reaction did not exceed 121 °C. After addition was complete, the reaction temperature was held at 93 °C for 60 minutes. Excess DIAMINE and xylene were distilled off at about 140 °C under about 1.5 mmHg. The reaction product had an amine value of about 207.5 mg KOH/g.

Subsequently, 44.18 g of Surfactant A, representing 0.009 equivalents, were charged to the flask at about 121 °C and heated to 200 °C for 2 hours. The reaction mixture was cooled to 93 °C, after which 180 g of HELOXY Modifier 62, representing 0.99 equivalents, were added to the reaction vessel at a rate such that the maximum temperature did not exceed 121 °C, after which the reaction was held at 93 °C for 60 minutes. The reaction mixture was allowed to cool to 78 °C. Water was added until the reaction mixture was inverted from a water in oil emulsion to an oil in water emulsion. The inversion occurred at 65% solids. Further water was added to reduce the level of solids to 50%. The emulsion was sheared until the average particle size was less than 2 microns.

EXAMPLE 2

150 g of Epoxy Resin A was hand mixed with 102.15 g of the water borne curing agent prepared according to

example 1 in the absence of external accelerator compounds, at an equivalent ratio of about 1:1, and allowed to cure at 75 °F and about 70% relative humidity. The mixture was drawn down on a Lemeta chart with a 2 mil Bird bar. The specular gloss pot life was 4-5 hours based on a 60° angle of incidence. The viscosity pot life was in excess of 6 and one-half hours. Thus, the water borne curing agent composition was compatible with the water borne epoxy resin composition, was self emulsifiable, and coalesced well as a film.

In the examples 3-7 the following reagents are used:

SSA is about 63 wt% salicyclic acid mono substituted with C_{14}-C_{18} alkyl groups dissolved in xylene and containing less than 15 mole% of C_{14}-C_{18} alkyl phenols and less than 5 mole% of dicarboxylic acid species, having an acid value of about 92 mg KOH/g in solution and about 146 mg KOH/g based on the solids.

TETA is triethylene tetramine commercially available from Union Carbide having a typical amine value of about 1436 mg KOH/g.

HELOXY Modifier 62

is a commercial grade of ortho-cresyl glycidyl ether manufactured by Shell Chemical Company, that is produced by treatment of ortho-cresol with epichlorohydrin and sodium hydroxide. HELOXY Modifier is a thin liquid having a viscosity at 25 °C of about 7 centipoise and an epoxide equivalent weight of about 175 to about 195.

SURFACTANT COMPOSITION B

is a glycidated block copolymer of ethylene oxide/propylene oxide having an internal block of

oxyalkylated propylene oxide to make an EO/PO/EO block having about 80% EO and 20% PO, wherein each end of the copolymer is glycidated. This glycidated block copolymer is mixed into EPON 828 at a weight ratio of 30/70 wt%, respectively.

EPON 828 RESIN

is a diglycidyl ether liquid epoxy resin commercially available from Shell Chemical Company.

EPOXY RESIN C

is an epoxy phenolic novolak dispersion in water having an average functionality of about 3.6.

EPOXY RESIN A

is a dispersion of an epoxy resin equivalent to EPON 1001 resin having an equivalent weight per epoxide group of about 450-550, in water having a functionality of less than 2.

EPI-REZ RESIN WD-510

is commercially available from Shell Chemical Company, and is an epoxy resin having a weight per epoxide group of about 190-205 dispersed in water (EPI-REZ is a trademark).

Example 3

This example illustrates the synthesis of the substituted aryl amidopolyamine compound based on a substituted salicyclic acid and triethylene tetramine, which is subsequently reacted with a monoglycidyl ether.

A 4 necked round-bottomed glass flask was equipped with a condenser having a water trap, a nitrogen inlet, an acid inlet, and the TETA inlet. The flask was flushed with nitrogen. 1529.4 g of SSA was charged to the flask, after which a total of 390.42 grams of TETA

was charged over a period of time to the flask, for a total of 1919.8 grams of reaction ingredients. The amount of SSA and TETA added were reacted in a ratio of one amine equivalent to one acid equivalent, or a 1:1 mole ratio. During the course of the reaction through completion, approximately 613 grams of water and xylene were distilled off. In this reaction scheme, the total amount of ingredients were mixed together prior to reaction.

After addition of the SSA was to the flask, TETA was added dropwise at about 23 °C initial, with the contents of the flask being stirred at about 60 rpm under a nitrogen pad, for a period of two hours, during which the exotherm raised the temperature of the reaction mixture to about 50 °C. Once addition of the TETA was complete, the temperature of the reactants in the flask was raised to 150 °C slowly over about a 55 minute period, and then raised to 160 °C over the next one and a half hours. The reaction was left overnight at room temperature. The next day, the reaction was again heated to 160 °C for the first two hours, and subsequently warmed to 170 °C over the next 7 hours. To drive the reaction to full completion and the desired acid value, the reactants were again heated to about 145 °C - 150 °C over a 5 hour period under vacuum at about 20 in.Hg. The acid value was measured at about 10.3 mg KOH/g, and the amine value was measured to be about 345.4 mg KOH/g.

Once this product was made, 514.82 grams of it was used to react with 198.25 g of the monoglycidyl ether HELOXY 62. The amounts of each ingredient used were based on reacting them in stoichiometric ratios of one primary amine equivalent to one epoxide equivalent.

The product was charged to a 4 necked round bottomed flask equipped with a condenser. The flask was purged with nitrogen, and agitation was initiated. Once the product was heated to 93 °C, the HELOXY 62 was added dropwise over a period of about 3 hours. The reaction temperature was held at 90-96 °C for the next 30 minutes, after which the final end capped amido-polyamine curing agent was isolated under nitrogen purge using a coarse grade Gardner filter cup. The acid and amine values of the final end capped amidopolyamine product were measured to be 7.6 and 246.4 mg KOH/g, respectively.

Example 4

This example demonstrates the manufacture of a high solids, water dispersed, self emulsifiable curing agent composition based upon the curing agent prepared in example 3.

The final end capped amidoamine product of example 3 was reacted with a glycidated surfactant in the following manner. 6.0 grams (about 1.8 grams of reactive surfactant) of Surfactant Composition B was added to 28.2 grams of the end capped amidoamine of example 1 in a 2 ounce glass jar on a heated hot plate under shear. This amount represents about 5.26 wt% of surfactant based on the weight of the solids in the final end capped amidoamine product of example 1. The reaction was allowed to proceed for 90 minutes at this temperature under agitation, and subsequently cooled to room temperature. At room temperature, the product was a tacky opaque solid which was warmed to a liquid and dispersed in 14.66 grams of water to achieve a 70% solids. The level of water was increased to obtain about a 57.6 % solids which was a cream coloured. Its

equivalent weight was about 260 g/eq based on solids and 450 g/eq as is, on a calculated basis.

The thixotropic emulsion was drawn down as a film on a Lenata chart. A clear glossy film was observed after 30-45 minutes. The thixotropic emulsion was stable.

Example 5

This example demonstrates the manufacture of a cured epoxy film using the water emulsion of example 4 as the water borne curing agent composition, in the absence of external accelerator compounds, and the specular gloss results obtained to indicate level of cure, compatibility, and film coalescence properties. An 80/20 wt% blend of epoxy resin A having 60 wt% solids and epoxy resin C having 66.5 wt% solids, respectively, had 61.3 wt% solids. On a draw down film on a Leneta chart, the epoxy resin blend produced a semi-glossy clear film in about 15 minutes. 11 grams of the thixotropic curing agent emulsion of example 2 having about 57.6 wt% of solids was added to 20 grams of this epoxy resin blend having 61.3% solids by hand mix for about 2-3 minutes, at a stoichiometric ratio of 1:1, and allowed to cure at ambient temperature.

Draw downs on Leneta charts were taken at 0, 30, 60, 130, 180, and 240 minute time intervals, each measured from t=0. The average specular glosses from the top, middle, and bottom of the films were recorded at incidence angles of 20° and 60°, reported below in Table 1.

Table 1

TIME (min)	20°	60°
0	71.8	97.9
30	71.1	96.8
60	66.7	97.3
130	54.5	92.8
180	49.6	92.6
240	23.1	70.4

The specular gloss values indicate the compatibility between the epoxy resin and curing agent composition, as well as predict the ability of the epoxy resin and the curing agent system to coalesce, thereby forming a high quality weatherable coating having more uniformity of thickness and density. It is desirable that the 60° specular gloss value is within 80% of its initial t=0 value at 180 minutes. More preferred are 60° specular gloss values retaining 80% of their initial value after 240 minutes. The 20° specular gloss values were also observed and recorded. 20° specular gloss values retaining 60% of their initial value after 180 minutes are good, and more preferred, the 60% value is retained up to 240 minutes.

The values reported in Table 1 above are each within the minimum 60% and 80% of their initial values at 180 minutes, indicating that the systems were compatible with each other, coalesced, and cured in the absence of external accelerators.

Example 6

This example demonstrates the curing ability of epoxy resins with the water borne curing agent composition of example 2, in the absence of external

accelerator compounds, and specular gloss obtained thereby. 57.6 wt% solids content were mixed together by hand and allowed to cure at 20 °C ± 2 °C and 30 ± 5% RH. The amounts grams and types of each ingredient are set forth below in Table 2.

Table 2

INGREDIENT	A*	B	C
EPOXY RESIN C	20.04	-	-
EPOXY RESIN A	-	33.5	-
80/20 wt BLEND A/C	-	-	29.79
CURING AGENT	29.96	16.5	20.21
% SOLIDS	57.12	58.38	58.78

*An additional 2.2 g of water was added upon mixing to adjust application rheology.

During the curing process, the specular gloss of each A-C sample was measured. The results are reported below in Table 3.

Table 3

TIME (min)	A		B		C	
	20°	60°	20°	60°	20°	60°
0	38.6	78.3	61.2	89.9	818	95.9
30	42.9	79.3	58.7	88.5	80	95.4
60	45.9	80.2	60.4	88.7	79.8	95.4
120	47.1	81.9	49.3	85.2	77.7	94.8
180	37.2	78.3	39.1	80.6	75	94.1
240	32.7	70.6	26.6	73.2	69.2	92.5
300	19	64.2	19.2	66.2	50.4	85.8

The specular gloss values were well within the 60% and 80% values at 240 minutes, except for the 20° specular gloss value of example B, which was within the 60% value at 180 minutes. These results indicate that the epoxy resin and curing agent were compatible, coalesced well to form a high quality film, and cured in the absence of external accelerators.

Example 7

This example demonstrates the manufacture of an epoxy film from a water borne epoxy resin and a water borne curing agent composition, in the absence of external accelerator compounds. A 50/50 blend by equivalents of Epoxy resin C and EPI-REZ resin WD510, diluted with water to yield 65% solids and an equivalent weight of about 315 as is, was prepared as the epoxy resin. The curing agent of example 4 was further diluted with water to yield 55% solids with an equivalent weight of 260 based on solids. 29.98 grams (16.49 grams based on solids) of the curing agent were hand mixed into 20.02 grams (13.01 based on solids) of

the epoxy resin to produce about system having about 59% solids. The mixture was allowed to cure, and the specular gloss was measured as in example 5. The results are reported in Table 4:

Table 4

TIME (min)	20°	60°
0	80.3	94.8
30	72.1	91.6
60	75.7	92.6
120	89.8	65.8
180	62	89.8
240	35.7	73.7

The values reported in Table 4 above are each within the minimum 60% and 80% of their initial values at 180 minutes, indicating that the systems were compatible with each other, coalesced, and cured in the absence of external accelerators.

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1. A stable water borne curing agent composition comprising a solid phase dispersed in a continuous phase comprising water, the solid phase comprising a curing agent composition and a surfactant composition, said surfactant composition comprising the reaction product of

a) a phenolic compound, substituted with at least one carboxyl group and at least one hydrocarbyl group having at least 1 carbon atom,

b) a polyamine compound having at least two primary amine groups,

c) a reactive surfactant, and optionally

d) a monoglycidyl, monocarboxylic acid or mono-isocyanate capping agent.

2. A stable water born curing agent composition according to claim 1, the surfactant composition in which comprises the reaction product of the components a), b), c) and optionally d) and in addition a polyepoxide compound e).

3. A stable water born curing agent composition according to claim 1, characterized in that the surfactant composition comprises the reaction product of a substituted aryl amidopolyamine, a d) monoglycidyl or monocarboxylic acid capping agent, and a c) reactive surfactant, said substituted aryl amidoamine comprising the reaction product of:

a) a phenolic compound substituted with at least one carboxyl group and at least one hydrocarbyl group having at least 1 carbon atom, and

* C L M S *

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b) a polyamine compound having at least two primary amine groups;

said reactive surfactant comprising a functional moiety reactive with secondary amines and a hydrophilic moiety of a nature and length effective to disperse the curing agent in water.

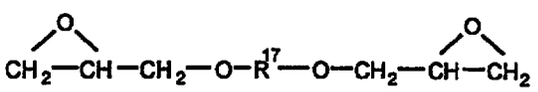
4. A stable water born curing agent composition of claim 2, characterized in that the phenolic acid compound with the polyepoxide compound to form a substituted aromatic glycidyl ester compound, and reacting the substituted aromatic glycidyl ester compound with at least the b) polyamine compound and the c) reactive surfactant.

5. The water borne curing agent composition of claim 2, wherein the carboxylic acid group(s) on said phenolic acid compound is reacted to substantial completion with the polyepoxide compound prior to reaction with the polyamine compound.

6. The water borne curing agent composition of claim 2, wherein the reaction between the polyepoxide compound and the phenolic acid are carried out at molar ratios of greater than 1:1, respectively.

7. The water borne curing agent composition of claim 2, wherein the polyepoxide has an average of 1.7 or more oxirane groups.

8. The water borne curing agent composition of claim 2, wherein the polyepoxide compound comprises a compound represented by the formulas:

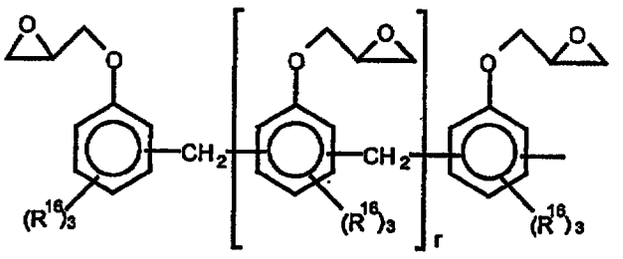


(XI)

or

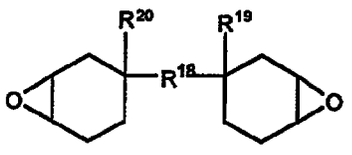
* C L M S *

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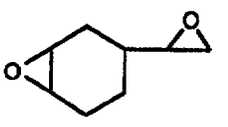


(XII)

or



(XIII) or



(XIV)

wherein r is a real number from about 0 to about 6, R^{17} is a divalent aliphatic group, a divalent cycloaliphatic group, a divalent aryl group, or a divalent aryl-aliphatic group;, R^{16} is independently a hydrogen or a C_1-C_{10} alkyl group; R^{18} is a divalent aliphatic group optionally containing ether or ester group(s) or together with R^{19} or R^{20} form a spiro ring optionally containing heteroatoms; and R^{19} and R^{20} are independently hydrogen or R^{19} or R^{20} together with R^{18} form a spiro ring optionally containing heteroatoms.

9. The water borne curing agent composition of claim 8, wherein the salicyclic acid is substituted with a branched or unbranched 14 to 24 carbon alkyl group.

10. The water borne curing agent composition of claim 5, wherein said substituted aromatic glycidyl ester compound is reacted with said polyamine compound to make a subsituted aromatic glycidyl ester - amine adduct, followed by

* C L M S *

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i) combining and reacting the d) capping agent with said substituted aromatic glycidyl ester - amine adduct to form a capped substituted aromatic glycidyl ester-amine adduct, followed by combining and reacting the c) reactive surfactant, or

ii) combining and reacting the substituted aromatic glycidyl ester-amine adduct with the c) reactive surfactant.

11. The water borne curing agent composition of claim 10, wherein at least one mole of the polyamine compound is reacted per mole of the substituted aromatic glycidyl esters.

12. The water borne curing agent composition of claim 1, wherein said functional moiety in the reactive surfactant comprise epoxide groups, carboxylic acid groups and anhydrides thereof, isocyanate groups, or mixtures thereof.

13. The water borne curing agent composition of claim 3, said surfactant composition comprising an end capped substituted aryl amidopolyamine made by reacting together a) and b) in a first step, and in a second step, reacting together said end capped substituted aryl amidopolyamine and said reactive surfactant, to form said reacted surfactant compound.

14. The water borne curing agent composition of claim 1, wherein the polyamine compound further contains at least one secondary amine group.

15. The water borne curing agent composition of claim 14, wherein the polyamine compound comprises diethylene triamine, triethylene tetramine, or m-xylylene diamine.

16. The water borne curing agent composition of claim 10, comprising a monoglycidyl capping agent, and

* C L M S *

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i) reacting the monoglycidyl capping agent with the said substituted aromatic glycidyl ester-amine adduct at a molar ratio of 0.5:1 to 2:1, respectively.

17. The water borne curing agent composition of claim 16, wherein the monoglycidyl ether comprises butyl glycidyl ether, cresyl glycidyl ether, phenyl glycidyl ether, nonylphenyl glycidyl ether, p-tert-butyl glycidyl ether, or an alkyl glycidyl ether having 8-16 branched or unbranched alkyl carbon atoms.

18. The water borne curing agent composition of claims 12 and 17, wherein the hydrophilic moiety in the reactive surfactant comprises a polyoxyalkylene monool or polyol residue.

19. The water borne curing agent composition of claim 18, comprising admixing the surfactant composition with the curing agent composition.

20. The water borne curing agent of claim 18, wherein the surfactant composition is formed in situ in the curing agent composition by:

iii) reacting the reactive surfactant with a stoichiometric excess of the curing agent composition, said curing agent composition comprising an end capped substituted aromatic glycidyl ester-amine adduct comprising the reaction product of said a), b), c), and e); or

iv) reacting the reactive surfactant with the c) polyamine compound, followed by reaction with a stoichiometric excess of a substituted aromatic glycidyl ester compounds made by reacting a) and b), followed by reacting at least a stoichiometric amount of a second portion of c) polyamine compound with the unreacted substituted aromatic glycidyl ester compounds to make a substituted aromatic glycidyl ester-amine

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adduct, and end capping at least a portion of unreacted primary amine groups remaining on said adduct with the e) capping agent.

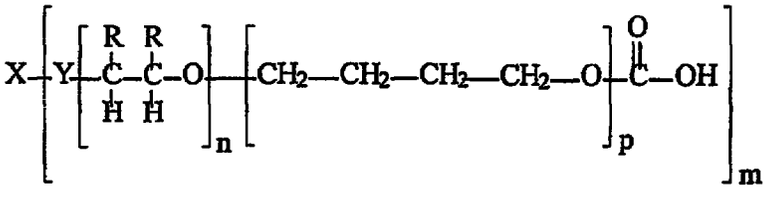
21. The water borne curing agent of claim 1, wherein the amount of surfactant composition in the stable water borne curing agent composition is from 1 wt% to 10 wt%, based on the weight of the solid phase, and the stable water borne curing agent composition comprises 45 wt% or more solids dispersed in the continuous phase, based on the weight of all ingredients in the water borne curing agent composition.

22. The water borne curing agent composition of claim 21, wherein the amount of surfactant composition comprises 2 to 6 wt%.

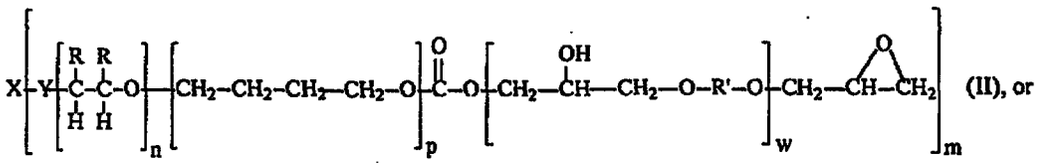
23. The water borne curing agent composition of claim 21, wherein the average particle size of the solid phase is 0.5 μ or less.

24. The water borne curing agent composition of claim 1, wherein the curing agent composition comprises an end capped substituted aromatic glycidyl ester-amine adduct comprising the reaction product of a), b), c), and e).

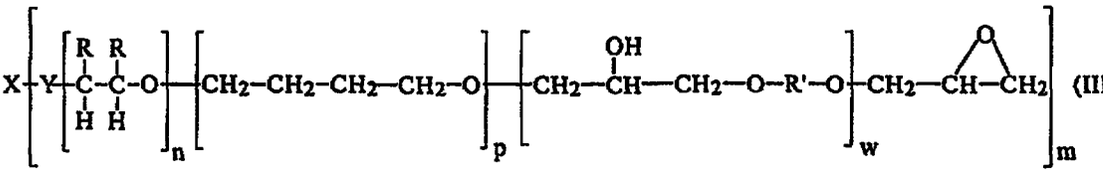
25. The water borne curing agent composition of claim 1, wherein the reactive surfactant comprises a compound represented by one of the following formulas:



(I), or



(II), or



(III)

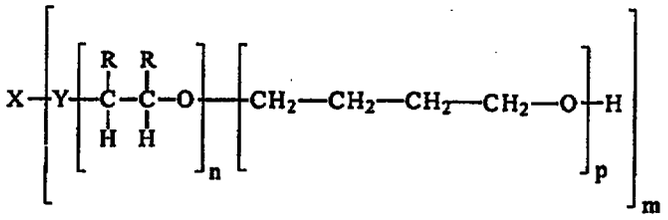
wherein X represents an initiator molecule residue, the initiator having a functionality of from 1 to 8; Y represents an oxygen or nitrogen atom; each of the R's independently represent a hydrogen, an C_1-C_{16} alkyl, aryl, or alkaryl group, provided that at least one R is a hydrogen; R' represents an epoxy resin residue comprising a divalent aliphatic group, a divalent cycloaliphatic group, a divalent aryl group, a divalent arylaliphatic group, or a divalent alkaryl group, each having from 2 to 1000 carbon atoms; m represents a real number from 1 to 8; n and p represent the number of repeating units of oxyalkylene groups effective to stably disperse the curing agent composition in water; and w represents the number of epoxy glycidyl ether units, ranging from 0 to 20.

26. The water borne curing agent composition of claim 25, wherein Y represents an oxygen atom, R represents hydrogen, methyl, or an ethyl group, provided that at least one R is hydrogen; m represents an integer from 1 to 3, each of n and p independently represent an integer such that n+p ranges from 15 to about 4000; and w represents an integer ranging from 0 to 5.

27. The water borne curing agent composition of claim 25, wherein the X, Y, n and p units are derived

* C L M S *

from a polyoxyalkylene monool or polyol represented by the formula:



28. The water borne curing agent composition of claim 27, wherein p is 0, and m is 1 or 2.

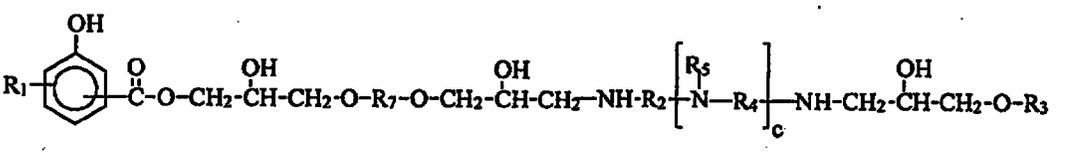
29. The water borne curing agent composition of claim 25, wherein the reactive surfactant comprises a molecule represented by formula II or III.

30. The water borne curing agent composition of claim 29, wherein the w ranges from greater than 0 to 5, and R' is derived from an epoxy resin having greater than 1.5 epoxide groups per molecule, said epoxy resin comprising a diglycidyl ether of a dihydric compound, an epoxy novolac, an aliphatic epoxy, or a cycloaliphatic epoxy.

31. The water borne curing agent composition of claim 1, comprising a cured epoxy resin comprising the reaction product of the water borne curing agent composition and a water borne epoxy resin composition in the absence of an external accelerator compound.

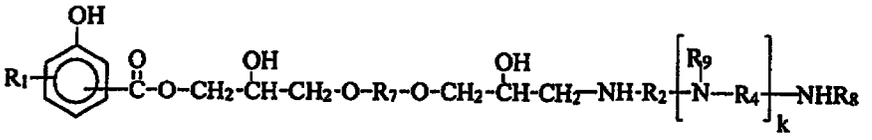
32. The water borne curing agent of claim 1, wherein said surfactant composition comprises a compound represented by at least one the following formulas:

* C L M S *



(V)

or



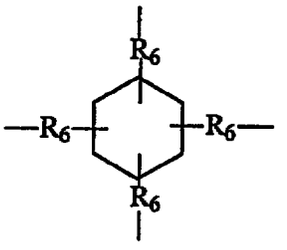
(VI)

wherein R_1 is a branched or unbranched, substituted or unsubstituted, monovalent hydrocarbyl group having at least on carbon atom; R_2 and R_4 each independently represent a branched or unbranched, substituted or unsubstituted, divalent hydrocarbyl group having 2-24 carbon atoms, or



(VII)

or



(VIII)

R_6 represents a branched or unbranched, substituted or unsubstituted, divalent hydrocarbyl group having 2-24 carbon atoms; R_3 is a branched or unbranched, substituted or unsubstituted, monovalent hydrocarbyl having 1-24 carbon atoms, an aryl group, an alkaryl group, or an aralkyl group; R_7 is the residue of said b) polyepoxide compound; R_5 and R_9 are each inde-

* C L M S *

pendently hydrogen, or a branched or unbranched, substituted or unsubstituted, alkyl group or alkaryl group or cycloaliphatic group, or the residue of said d) reactive surfactant; R_8 is the residue of said d) reactive surfactant; c represents an integer from 1-10; and k represents an integer from 0-10; provided that at least one R_5 group is said the residue of said d) reactive surfactant.

33. The water borne curing agent of claim 32, wherein the carbon number of the group represented by R_1 is greater than 12, c is an integer from 1-4, and k is an integer from 0-4.

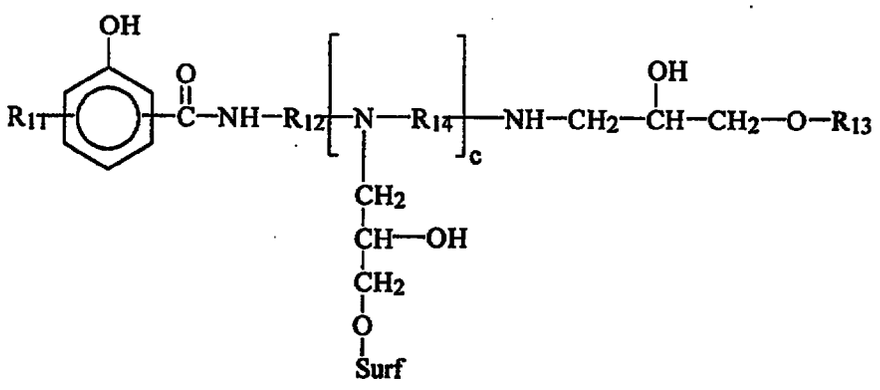
34. The water borne curing agent of claim 33, wherein the polyamine compound comprises diethylene triamine, triethylene tetramine, m-xylylene diamine, or an aliphatic diamine.

35. The water borne curing agent of claim 32, wherein R_3 comprises the residue of an alkyl glycidyl ether having 2-18 carbon atoms or an alkaryl glycidyl ether wherein the alkyl has 1-24 carbon atoms.

36. The water borne curing agent of claim 32, wherein R_3 comprises the residue of butyl glycidyl ether, cresyl glycidyl ether, phenyl glycidyl ether, nonyl-phenyl glycidyl ether, p-tert-butyl glycidyl ether, or an alkyl glycidyl ether having 8-16 branched or unbranched alkyl carbon atoms.

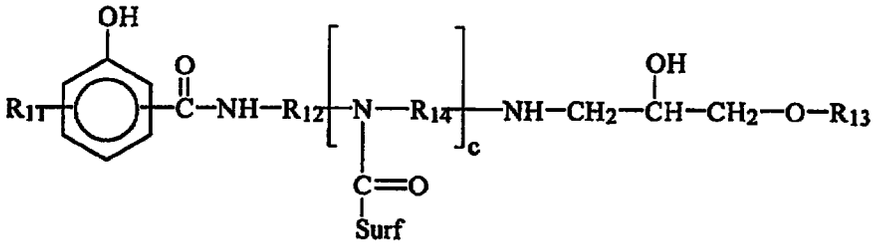
37. The water borne curing agent of claim 2, wherein said surfactant composition comprises a reacted surfactant compound comprising a compound represented by at least one the following formulas:

* C L M S *



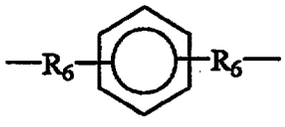
(IX)

or

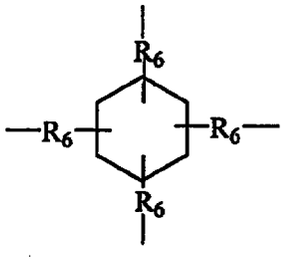


(X)

wherein R_{11} is a branched or unbranched, substituted or unsubstituted, monovalent hydrocarbyl group having at least on carbon atom; R_{12} and R_{14} each independently represent a branched or unbranched, substituted or unsubstituted, divalent hydrocarbyl group having 2-24 carbon atoms, or



or



R_6 represents a branched or unbranched, substituted or unsubstituted, divalent hydrocarbyl group having 2-24 carbon atoms; R_{13} is a branched or unbranched, substituted or unsubstituted, monovalent hydrocarbyl having 1-24 carbon atoms, an aryl group, an alkaryl group, or an aralkyl group; c represents an integer from 0-10; and Surf represents the c) reactive surfactant residue; provided that when c=0, the -CO-Surf group and the $-CH_2-CHOH-CH_2-O$-Surf group are bonded to the nitrogen atom farthest from the depicted amide group.

38. The water borne curing agent of claim 37, wherein the carbon number of the group represented by R_{11} is greater than 12, and c is an integer from 1-10.

39. The water borne curing agent of claim 38, wherein the polyamine compound comprises diethylene triamine, triethylene tetramine, or m-xylylene diamine.

40. A surfactant composition comprising the reaction product of:

a) a phenolic acid compound substituted with at least one carboxyl group and at least one hydrocarbyl group having at least 1 carbon atom;

b) a polyamine compound having at least two primary amine groups;

c) a reactive surfactant; and optionally

d) a monoglycidyl, monocarboxylic acid, or monoisocyanate capping agent;

said reactive surfactant comprising a functional moiety reactive with secondary amines and a hydrophilic moiety of a nature and length effective to disperse the curing agent in water.

41. A surfactant composition according to claim 40, characterized in that it comprises the reaction product

* C L M S *

of the components a), b), c) and optionally d) and in addition a polyepoxide compound e).

42. A surfactant composition according to claim 40, characterized in that it comprises a reacted surfactant compound comprising the reaction product of a substituted aryl amidopolyamine, a monoglycidyl or monocarboxylic acid capping agent, and a c) reactive surfactant, said substituted aryl amidoamine comprising the reaction product of:

a) a phenolic compound substituted with at least one carboxyl group and at least one hydrocarbyl group having at least 1 carbon atom, and

b) a polyamine compound having at least two primary amine groups;

said reactive surfactant comprising a functional moiety moiety reactive with secondary amines and a hydrophilic moiety of a nature and length effective to disperse the curing agent in water.

* C L M S *