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<p>(54) Title: AN ACID-EPOXY-MELAMINE COATING COMPOSITION MODIFIED WITH A SILANE POLYMER</p>		
<p>(57) Abstract</p> <p>A coating composition useful for a finish for automobiles and trucks in which the film forming binder comprises an acrylic polymer having at least two reactive acid groups, an epoxy-containing crosslinker, a melamine resin, and an epoxy-silane modifying agent. The composition may be used as a one-package system with a reasonable pot life. The composition is characterized by improved environmental resistance.</p>		

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**TITLE****AN ACID-EPOXY-MELAMINE COATING COMPOSITION  
MODIFIED WITH A SILANE POLYMER**

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**FIELD OF THE INVENTION**

This invention is related to a coating composition comprising an acid-epoxy-melamine composition modified with a silane polymer.

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**BACKGROUND**

There are a wide variety of coating compositions available for finishing automobiles and trucks. Various coating compositions comprising anhydride-epoxy or acid-epoxy containing compositions are known. For example, U.S. Patent 4,906,677 discloses a composition comprising an acrylic anhydride polymer, a glycidyl component, and a phosphonium catalyst. U.S. patent 4,681,811 discloses a composition comprising a polyepoxide and a polyacid curing agent.

A problem with present coating compositions for automobiles and trucks, or parts thereof, is that durability is not as good as desired. An important aspect of durability is environmental resistance. The present invention offers a high quality finish exhibiting superior environmental resistance. Another problem with epoxy-containing systems has been that, due to limited pot life, they have been used as a two package system, which packages are conventionally mixed shortly before use. The present composition is a potential one-package system. Such a coating composition exhibits excellent adhesion to the substrate to which it is applied, good outdoor weatherability, etch resistance, and gloss.

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**SUMMARY OF THE INVENTION**

An essentially anhydride-free coating composition containing 20-80% by weight of binder components and 80-20% by weight of solvent. The binder contains, as separate molecules or components of the mixture, the following:

- (a) an acid polymer having at least two acid (carboxyl) groups and having a weight average molecular weight of about 2,000-50,000;
- (b) an epoxy component having at least two reactive glycidyl groups;
- (c) a melamine crosslinker;
- (d) an acrylosilane polymer; and
- (e) an effective amount of a curing catalyst.

In one embodiment of the invention, the acrylosilane polymer has reactive epoxy groups as well as silane groups.

#### DETAILED DESCRIPTION OF THE INVENTION

The composition of the present invention forms a durable environmental resistant coating. The composition is especially useful for finishing the exterior of automobiles and trucks.

The composition can also be pigmented to form a colored finish, although the composition is especially useful as a clearcoat.

Preferably, the coating composition has a high solids content and contains about 20-80% by weight binder and 20-80% by weight of organic solvent. The binder of the composition contains about 25-90%, preferably 35 to 65% by weight of binder, of an acid polymer containing at least two anhydride groups; 5-30%, preferably 10 to 20% by weight of binder, of a glycidyl containing component; 5-30%, preferably 10-20% of polymer comprising silane groups and optionally epoxy groups; and 2-15% of a polymeric melamine resin, preferably 3-9% by weight of binder.

Optionally, the composition may, in addition, comprise 5-30%, preferably 10 to 25% by weight of binder of an acrylic or a polyester or a polyester urethane which may contain hydroxyl and/or acid functionality. If hydroxy functional, the hydroxy number is 20 to 120. If acid functional, the acid number is 20 to 120. The binder should contain a maximum of 25%, based on the weight of the binder of aromatic vinyl.

The acid polymer employed in preparing the present composition has a weight average molecular weight of about 2,000-50,000, determined by gel permeation chromatography using polymethyl

methacrylate as a standard. Preferably the anhydride polymer has a weight average molecular weight of 3,000-25,000.

The acid polymer may be prepared by conventional techniques in which the monomers, solvent, and conventional catalysts such as t-butyl perbenzoate are charged into a polymerization vessel and heated to about  
5 75-200°C for about 0.5-6 hours to form the polymer.

The acid polymer can be formed by polymerizing monomers of alkyl methacrylates, or alkyl acrylates or mixtures thereof, where the alkyl groups have 1-12 carbon atoms, preferably 1-6 carbon atoms, and  
10 ethylenically unsaturated acids. Optionally, the acid functional polymer can also contain other components such as styrene, methyl styrene, and/or acrylonitrile, methacrylonitrile in amounts of about 0.1-50% by weight.

Typically useful ethylenically unsaturated acids are acrylic acid, methacrylic acid, itaconic acid, maleic acid, isobutenyl succinic acid, and the  
15 like.

This acid resin may also contain hydroxyl functionality by using monomers such as hydroxyethylacrylate, hydroxyethyl methacrylate and hydroxypropyl acrylate. The hydroxy functionality may be introduced by a post reaction of the acid with epoxy containing compounds such as  
20 Cardura E® from Shell Chemical Company (a glycidyl ester of versatic acid) and propylene oxide.

Typical alkyl acrylates and methacrylates that can be used to form the acid acrylic polymer are methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, isobutyl methacrylate, pentyl  
25 methacrylate, hexyl methacrylate, octyl methacrylate, nonyl methacrylate, decyl methacrylate, lauryl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, octyl acrylate, nonyl acrylate, decyl acrylate, lauryl acrylate, and the like. Cycloaliphatic methacrylates and acrylates also can be used, for example, such as trimethylcyclohexyl methacrylate,  
30 trimethylcyclohexyl acrylate, iso-butyl methacrylate, t-butyl cyclohexyl acrylate, or t-butyl cyclohexyl methacrylate. Aryl acrylate and aryl methacrylates also can be used, for example, such as benzyl acrylate and benzyl methacrylate. Of course, mixtures of the two or more of the above mentioned monomers are also suitable.

Other components that can be used to form the acid acrylic polymer are acrylamide and methacrylamide.

It is also possible to impart the acid functionality to the acid acrylic polymer by using an ethylenically unsaturated acid anhydride which  
5 can be converted completely or substantially completely to the corresponding acid polymer.

A preferred acid acrylic polymer comprises styrene, butyl methacrylate, n-butyl acrylate, and methacrylic acid.

The epoxy component preferably contains at least two glycidyl  
10 groups and can be an oligomer or a polymer. Typical glycidyl components are sorbitol polyglycidyl ether, mannitol polyglycidyl ether, pentaerythritol polyglycidol ether, glycerol polyglycidyl ether, low molecular weight epoxy resins such as epoxy resins of epichlorohydrin and bisphenol A, di- and polyglycidyl esters of acids, polyglycidyl ethers of isocyanurates, such as  
15 Denecol EX301® from Nagase. Sorbitol polyglycidyl ethers, such as DCE-358® from Dixie, Inc., and di- and polyglycidyl esters of acids, such as Araldite CY-184® from Ciba-Geigy or XUS-71950® from Dow Chemical form high quality finishes. Cycloaliphatic epoxies such as CY-179® from Ciba-Geigy may also be used.

20 Glycidyl methacrylate or acrylate containing acrylic polymers can be used, such as random and block polymers of glycidyl methacrylate/butyl methacrylate. The block polymers can be prepared by anionic polymerization or by group transfer polymerization.

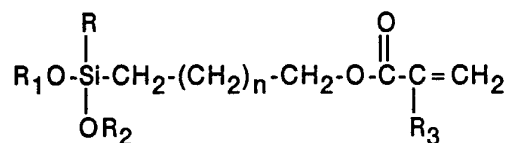
The melamine crosslinker is suitably a conventionally known  
25 alkylated melamine formaldehyde resin that is partially or fully alkylated, for example a methylated and butylated or isobutylated melamine formaldehyde resin that has a degree of polymerization of about 1-5. Polymeric melamines are preferred because they are catalyzed by weak acids such as carboxylic acids versus strong acids such as sulfonic acids and are not  
30 hindered by amines.

The silane polymer portion of the binder has a weight average  
molecular weight of about 1000 to 30,000. (All molecular weights disclosed  
herein are determined by gel permeation chromatography using a  
polystyrene standard.) The silane polymer is suitably the polymerization  
35 product of about 5-70%, preferably 40-60%, by weight of polymer, of

ethylenically unsaturated silane containing monomers, and 30-95%, preferably 40-60%, by weight of non-silane containing monomers. Suitably non-silane containing monomers are the alkyl acrylates and alkyl methacrylates mentioned above with respect to the acid polymer, as well as styrene, methyl styrene, acrylamide, acrylonitrile, methacrylonitrile, and the like.

In addition to alkyl acrylates or methacrylates, other non-silane-containing polymerizable monomers, up to about 50% by weight of the polymer, can be used in an acrylosilane polymer for the purpose of achieving the desired physical properties such as hardness, appearance, mar resistance, and the like. Exemplary of such other monomers are styrene, methyl styrene, acrylamide, acrylonitrile, methacrylonitrile, and the like. Styrene can be used in the range of 0-50% by weight.

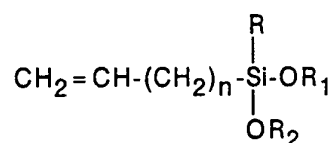
A suitable silane containing monomer useful in forming an acrylosilane polymer is an alkoxy silane having the following structural formula:



wherein R is either CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>, CH<sub>3</sub>O, or CH<sub>3</sub>CH<sub>2</sub>O; R<sub>1</sub> and R<sub>2</sub> are CH<sub>3</sub> or CH<sub>3</sub>CH<sub>2</sub>; R<sub>3</sub> is either H, CH<sub>3</sub>, or CH<sub>3</sub>CH<sub>2</sub>; and n is 0 or a positive integer from 1 to 10. Preferably, R is CH<sub>3</sub>O or CH<sub>3</sub>CH<sub>2</sub>O and n is 1.

Typical examples of such alkoxy silanes are the acryloalkoxy silanes, such as gammaacryloxypropyltrimethoxy silane and the methacryloalkoxy silanes, such as gamma-ethacryloxypropyltrimethoxy silane, and gamma-methacryloxypropyltris(2-methoxyethoxy) silane.

Other suitable alkoxy silane monomers have the following structural formula:



wherein R, R<sub>1</sub> and R<sub>2</sub> are as described above and n is a positive integer from 1 to 10.

Examples of such alkoxysilanes are the vinylalkoxy silanes, such as vinyltrimethoxy silane, vinyltriethoxy silane and  
5 vinyltris(2-methoxyethoxy) silane.

Other suitable silane containing monomers are acyloxysilanes, including acrylatoxy silane, methacrylatoxy silane and vinylacetoxysilanes, such as vinylmethyl diacetoxysilane, acrylatopropyl triacetoxysilane, and methacrylatopropyltriacetoxysilane. Of course, mixtures of the  
10 above-mentioned silane-containing monomers are also suitable.

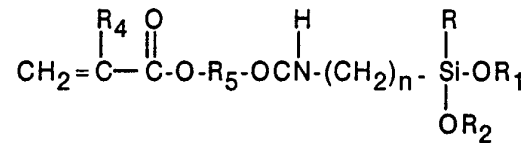
Consistent with the above mentioned components of the silane polymer, an example of an organosilane polymer useful in the coating composition of this invention may contain the following constituents: about 15-25% by weight styrene, about 30-60% by weight  
15 methacryloxypropyltrimethoxy silane, and about 25-50% by weight trimethylcyclohexyl methacrylate.

One preferred acrylosilane polymer contains about 30% by weight styrene, about 50% by weight methacryloxypropyltrimethoxy silane, and about 20% by weight of nonfunctional acrylates or methacrylates such as  
20 trimethylcyclohexyl methacrylate, butyl acrylate, and iso-butyl methacrylate and any mixtures thereof.

Silane functional macromonomers also can be used in forming the silane polymer. These macromonomers are the reaction product of a silane containing compound, having a reactive group such as epoxide or  
25 isocyanate, with an ethylenically unsaturated non-silane containing monomer having a reactive group, typically a hydroxyl or an epoxide group, that is co-reactive with the silane monomer. An example of a useful macromonomer is the reaction product of a hydroxy functional ethylenically unsaturated monomer such as a hydroxyalkyl acrylate or methacrylate having  
30 1-4 carbon atoms in the alkyl group and an isocyanatoalkyl alkoxysilane such as isocyanatopropyl triethoxysilane.

Typical of such above mentioned silane functional macromonomers are those having the following structural formula:





wherein R, R<sub>1</sub>, and R<sub>2</sub> are as described above; R<sub>4</sub> is H or CH<sub>3</sub>, R<sub>5</sub> is an alkylene group having 1-8 carbon atoms and n is a positive integer from 1-8.

5 Curing catalysts for catalyzing the crosslinking between silane moieties of a silane polymer and/or between silane moieties and other components of the composition include dibutyl tin dilaurate, dibutyl tin diacetate, dibutyl tin dichloride, dibutyl tin dibromide, triphenyl boron, tetraisopropyl titanate, triethanolamine titanate chelate, dibutyl tin dioxide,  
 10 dibutyl tin dioctoate, tin octoate, aluminum titanate, aluminum chelates, zirconium chelate, and other such catalysts or mixtures thereof known to those skilled in the art. Tertiary amines and acids or combinations thereof are also useful for catalyzing silane bonding.

In one embodiment of the present invention, the silane  
 15 polymer optionally also has epoxy groups, that is, a portion of the monomers reacted to form the polymer contain an epoxy group. An example of a suitable epoxy functional monomer is glycidyl methacrylate and the like. Suitably, the silane polymer may be the reaction product of a monomer mixture comprising up to 40% by weight of an epoxy functional monomer,  
 20 preferably 5 to 20%, and most preferably 10 to 15% by weight of an epoxy functional monomer.

As indicated above, the binder of the present composition may further comprise from about 5 to 30%, preferably 10 to 25%, based on the weight of the binder, of an acrylic or polyester or a polyester urethane or  
 25 copolymer thereof having a hydroxy number of about 20 to 120, preferably 70 to 100, or an acid number of about 20 to 120, preferably 75 to 95. This polymer has a weight average molecular weight of about 2,000 to 20,000, preferably 4,000-10,000. Unless otherwise indicated, all molecular weights mentioned herein are measured using gel permeation chromatography using  
 30 polymethyl methacrylate as a standard.

Polyester urethanes are a reaction product of a hydroxyl terminated polyester component and a polyisocyanate component, preferably, an aliphatic or cycloaliphatic diisocyanate. A polyester, which

may be used alone or as a component of the polyester urethane, may be suitably prepared from linear or branched chain diols, including ether glycols, or mixtures thereof or mixtures of diols and triols, containing up to and including 8 carbon atoms, or mixtures of such diols, triols, and  
5 polycaprolactone polyols, in combination with a dicarboxylic acid, or anhydride thereof, or a mixture of dicarboxylic acids or anhydrides, which acids or anhydrides contain up to and including 12 carbon atoms, wherein at least 75% by weight, based on the weight of dicarboxylic acid, is an aliphatic dicarboxylic acid.

10 Representative saturated and unsaturated polyols that can be reacted to form a polyester include alkylene glycols such as neopentyl glycol, ethylene glycol, propylene glycol, butane diol, pentane diol, 1,6-hexane diol, 2,2-dimethyl-1,3-dioxolane-4-methanol, 1,4-cyclohexane dimethanol, 2,2-dimethyl 1,3-propanediol, 2,2-bis(hydroxymethyl)propionic acid, and  
15 3-mercapto-1,2-propane diol. Preferred are 1,6-hexanediol and butylene glycol.

Polyhydric alcohols, having at least three hydroxyl groups, may also be included to introduce branching in the polyester. Typical polyhydric alcohols are trimethylol propane, trimethylol ethane, pentaerythritol, glycerin  
20 and the like. Trimethylol propane is preferred, in forming a branched polyester.

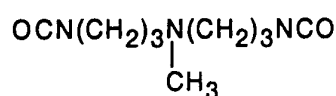
Polycaprolactone polyols may be also be used in making the polyester. A preferred polycaprolactone, a triol, is Tone® FCP 310 (available from Union Carbide).

25 The carboxylic acids used in making the polyester component of the polyester urethane include the saturated and unsaturated polycarboxylic acids and the derivatives thereof. Aliphatic dicarboxylic acids that can be used to form the polyester are as follows: adipic acid, sebacic acid, succinic acid, azelaic acid, dodecanedioic acid, 1,3 or 1,4-cyclohexane  
30 dicarboxylic acid and the like. A preferred acid is adipic acid. Aromatic polycarboxylic acids include phthalic acid, isophthalic acid, terephthalic acid, and the like. Anhydrides may also be used, for example, maleic anhydride, phthalic anhydride, trimellitic anhydride, and the like.

Typical polyisocyanates that may be used to form the polyester urethane are as follows: isophorone diisocyanate which is  
35

3-isocyanatemethyl-3,5,5-trimethyl- cyclohexyl-isocyanate,  
propylene-1,2-diisocyanate, butylene-1,2-diisocyanate,  
butylene-1,3-diisocyanate, hexamethylene diisocyanate,  
methyl-2,6-diisocyanate, methyl-2,6-diisocyanate caproate, octamethylene  
5 diisocyanate, 2,4,4-trimethylhexamethylene diisocyanate, nonamethylene  
diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate, decamethylene  
diisocyanate, 2,11-diisocyno-dodecane and the like, meta-phenylene  
diisocyanate, para-phenylene diisocyanate, toluene-2, 4-diisocyanate,  
toluene-2,6-diisocyanate, xylene-2, 4-diisocyanate, xylene-2,6-diisocyanate,  
10 dialkyl benzene diisocyanates, such as methylpropylbenzene diisocyanate,  
methylethylbenzene diisocyanate, and the like: 2,2'-biphenylene  
diisocyanate, 3,3'-biphenylene diisocyanate, 4,4'-biphenylene diisocyanate,  
3,3'-dimethyl-4,4'-biphenylene diisocyanate, and the like;  
methylene-bis(4-phenyl isocyanate), ethylene-bis(4-phenyl isocyanate),  
15 isopropylidene-bis(4-phenyl isocyanate), butylene-bis(4-phenylisocyanate),  
and the like; 2,2'-oxydiphenyl diisocyanate, 3,3'-oxydiphenyl diisocyanate,  
4,4'-oxydiphenyl diisocyanate, 2,2'-ketodiphenyl diisocyanate,  
3,3'-ketodiphenyl diisocyanate, 4,4'-ketodiphenyl diisocyanate,  
2,2'-thiodiphenyl diisocyanate, 3,3'-thiodiphenyl diisocyanate,  
20 4,4'-thiodiphenyl diisocyanate, and the like; 2,2'-sulfonediphenyl  
diisocyanate, 3,3'-sulfonediphenyl diisocyanate, 4,4'-sulfonediphenyl  
diisocyanate, and the like; 2,2,-methylene-bis(cyclohexyl isocyanate),  
3,3'-methylene-bis(cyclohexyl isocyanate), 4,4'-methylene-bis(cyclohexyl  
isocyanate), 4,4'-ethylene-bis(cyclohexyl isocyanate),  
25 4,4'-propylene-bis-(cyclohexyl isocyanate),  
bis(para-isocyano-cyclohexyl)sulfide, bis(para-isocyano-cyclohexyl)sulfone,  
bis(para-isocyano-cyclohexyl)ether, bis(para-isocyano-cyclohexyl)diethyl  
silane, bis(para-isocyano-cyclohexyl)diphenyl silane,  
bis(para-isocyano-cyclohexyl)ethyl phosphine oxide,  
30 bis(para-isocyano-cyclohexyl)phenyl phosphine oxide,  
bis(para-isocyano-cyclohexyl)N-phenyl amine,  
bis(para-isocyano-cyclohexyl)N-methyl amine, 3,3'-dimethyl-4,4'-diisocyno  
biphenyl, 3,3'-dimethoxy-biphenylene diisocyanate,  
2,4-bis(b-isocyano-t-butyl)toluene, bis(para-b-isocyano-t-butyl-phenyl)ether,  
35 para-bis(2-methyl-4-isocyanophenyl)benzene, 3,3-diisocyno adamantane,

3,3-diisocyano biadamantane, 3,3-diisocyanoethyl-1'-biadamantane,  
 1,2-bis(3-isocyano-propoxy)ethane, 2,2-dimethyl propylene diisocyanate,  
 3-methoxy-hexamethylene diisocyanate 2,5-dimethyl heptamethylene  
 diisocyanate, 5-methyl-nonamethylene diisocyanate,  
 5 1,4-diisocyano-cyclohexane, 1,2-diisocyano-octadecane,  
 2,5-diisocyano-1,3,4-oxadiazole,  $\text{OCN}(\text{CH}_2)_3\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_3\text{NCO}$ ,  
 $\text{OCN}(\text{CH}_2)_3\text{NCO}$  or the following:



10

Aliphatic diisocyanates are preferred, forming urethanes that have excellent weatherability. One aliphatic diisocyanate that is particularly preferred is trimethyl hexamethylene diisocyanate.

15 A preferred polyester urethane is the reaction product of trimethylhexamethylene diisocyanate and a hydroxy terminated polyester of 1,3-butylene glycol, 1,6-hexanediol, adipic acid, trimethylolpropane, and Tone® FCP 310.

20 It is noted that a hydroxy functional polyester urethane can be converted to the corresponding acid functional polyester urethane by reaction with methylhexahydrophthalic anhydride or other mono-anhydride such as succinic anhydride. Converting the hydroxy to the acid may result in longer pot life.

25 A polyester may be prepared by conventional techniques in which the component polyols and carboxylic acids and solvent are esterified at about 110°C-250°C for about 1-10 hours to form a polyester. To form a polyester urethane, a diisocyanate may then be added and reacted at about 100°C for about 15 minutes to 2 hours.

30 In preparing the polyester urethane, a catalyst is typically used. Conventional catalysts include benzyl trimethyl ammonium hydroxide, tetramethyl ammonium chloride, organic tin compounds, such as dibutyl tin diaurate, dibutyl tin oxide stannous octoate and the like, titanium complexes and litharge. About 0.1-5% by weight of catalyst, based on the total weight of the reactants, is typically used.

The stoichiometry of the polyester preparation is controlled by the final hydroxyl number and by the need to obtain a product of low acid number; an acid number below 10 is preferable. The acid number is defined as the number of milligrams of potassium hydroxide needed to neutralize a 1 gram sample of the polyester. Additional information on the preparation of polyester urethanes is disclosed in commonly assigned U.S. Patent No. 4,810,759, hereby incorporated by reference.

Another optional component of the present composition is the half ester of an anhydride compound, as distinguished from a polymer, for example the reaction product of an acid anhydride such as hexahydrophthalic anhydride or a succinic anhydride, which may be substituted, for example with a C<sub>1</sub>-C<sub>8</sub> alkyl group, with a monofunctional or polyfunctional alcoholic solvent such as methanol or ethylene glycol. A preferred half ester is the reaction product of methylhexahydrophthalic anhydride and an alcohol. Other alcoholic solvents are propanol, isobutanol, isopropanol, tertiary butanol, n-butanol, propylene glycol monomethyl ether, ethylene glycol monobutyl ether, and the like. Such half esters are useful for boosting the solids content of the composition. More particularly, such a half ester is chosen to be a good solvent for the preferred phosphonium catalyst. The half ester is suitably present in the amount of 2 to 25 percent by weight of binder, preferably 4-12 percent.

About 0.1-5% by weight, based on the weight of the binder of the coating composition, of a catalyst is added to enhance curing of the composition. Typical catalysts are as follows: triethylene diamine, quinuclidine, dialkyl alkanol amines such as dimethyl ethanolamine, diethyl ethanol amine, dibutyl ethanol amine, diethyl hexanol amine and the like, lithium tertiary butoxide, tri(dimethylaminomethyl)phenol, bis(dimethylamino)propan-2-ol, N,N,N<sup>1</sup>,N<sup>1</sup>-tetramethylethylenediamine, N-methyldiethanolamine, N,N-dimethyl-1,3-propanediamine and 1-dimethylamino-2-propanol or quaternary ammonium salts such as tert-butyl ammonium bromide, benzyl trimethyl ammonium formate and the like. Preferred catalyst, however, are phosphonium compounds such as are disclosed in U.S. Patent No. 4,906,677, hereby incorporated by reference in its entirety.

Typical solvents used as a diluent for the coating composition include toluene, xylene, butyl acetate, ethyl benzene, higher boiling aromatic hydrocarbons, amyl acetate, ethyl acetate, propyl acetate, ethylene or propylene glycol mono alkyl ether acetates.

5 Generally, the present composition is applied as a coating to a substrate by conventional techniques such as spraying and electrostatic spraying. The composition may be applied as a one-package system. The resulting coating can be dried and cured at elevated temperatures of 100 to 200°C. Coatings are applied to form a finish typically about 0.5-5 mils thick,  
10 and preferably 1-2 mils thick.

To improve the pot life or stability of the composition it is desirable to include a trialkyl orthoacetate or orthoformate, wherein the alkyl group has 1-6 carbon atoms. Preferred compounds are trimethyl or triethyl orthoacetate. A suitable range of such a stabilizer is 1 to 6% by  
15 weight of composition, preferably about 3 to 4% by weight. Such a stabilizer also serves to keep the viscosity of the composition low.

To improve weatherability of the clear finish of the coating composition, about 0.1-5%, by weight, based on the weight of the binder, of an ultraviolet light stabilizer or a combination of ultraviolet light stabilizers  
20 can be added. These stabilizers include ultraviolet light absorbers, screeners, quenchers and specific hindered amine light stabilizers. Also, about 0.1-5% by weight, based on the weight of the binder, of an antioxidant can be added.

Typical ultraviolet light stabilizers that are useful are listed in U.S. patent no. 4,906,677, previously incorporated by reference. Particularly  
25 useful ultraviolet light stabilizers that can be used are hindered amines of piperidyl derivatives such as those disclosed in Murayama et al., U.S. Patent 4,061,616, issued December 6, 1977, column 2, line 65, through column 4, line 2, and nickel compounds such as  
[1-phenyl-3-methyl-4-decanoylpyrazolate(5)]-Ni,  
30 bis[phenyldithiocarbamate]-Ni(II), and others listed in the above patent, column 8, line 44 through line 55.

An applicable blend of ultraviolet light stabilizers comprises 2-[2'-hydroxy-3',5'-1(1-1-dimethyl-propyl)phenyl]benzotriazole and bis-[4-(1,2,2,6,6-pentamethylpiperidyl)] 2-butyl-2-[(3,5-t-butyl-4-hydroxy-

phenyl)methyl] propanedioate. Although the stabilizers can be employed in any ratio, a 1:1 ratio of benzotriazole to propanedioate is preferred.

The composition can be pigmented to form a colored finish or primer. About 0.1-200% by weight, based on the weight of the binder, of  
 5 conventional pigments can be added using conventional techniques in which a mill base containing pigment, dispersant and solvent is first formed. The mill base is then mixed with the composition to form a colored composition. This composition can be applied and cured as shown above.

The present composition can be used in a one-package system  
 10 with a pot life of up to several weeks, depending on conditions.

The following examples illustrate the invention. All parts and percentages are on a weight basis unless otherwise indicated. The weight average molecular weight of polymers was determined by GPC (gel permeation chromatography) using polyethyl methacrylate as a standard,  
 15 unless stated otherwise.

EXAMPLE 1

This example illustrates, as a component for use in the present composition, an acid polymer, more specifically a methacrylic acid resin,  
 20 which may be prepared by charging the following constituents into a reactor equipped with a thermometer, stirrer, dropping funnel, and condensor:

	<u>Portion 1</u>	<u>Parts by Weight</u>
	Propylene glycol monomethyl ether acetate	155.3
25	(PM acetate)	
	Xylene	103.5
	<u>Portion 2</u>	
	n-Butyl methacrylate	174.8
	Methacrylic acid	97.1
30	Butyl acrylate	140.8
	Styrene	72.8
	<u>Portion 3</u>	
	Tertiarybutyl peroxyacetate	35.0
	Propylene glycol monomethyl ether acetate	41.7
35	(PM acetate)	

Xylene	<u>27.8</u>
Total	849.0

5 Portion 1 was charged into the reactor and heated to its reflux (approximately 140°C). Portion 2 was premixed and added to the reactor dropwise over a 240 minute period. Portion 3 was premixed and added to the reactor over a 270 minute period concurrent with Portion 3. After the addition was complete, the reactor was held at reflux and filled out.

10 The resulting acid polymer composition had a composition of 15% styrene, 36% butyl methacrylate, 29% n-butyl acrylate, and 20% methacrylic acid. The solids content was 60% and the polymer had a Gardner-Holdt viscosity of Z-1. The polymer had a weight average molecular weight of 5000.

#### 15 EXAMPLE 2

This example illustrates one embodiment of an acrylosilane polymer which may be employed in a composition according to the present invention. A solution of the polymer is prepared by charging the following constituents into a polymerization reactor equipped with a heat source and a reflux condenser:

	<u>Parts by</u> <u>Weight</u>
<u>Portion I</u>	
"Solvesso" 100	75.00
<u>Portion II</u>	
Methacryloxypropyltrimethoxy silane	300.00
Styrene monomer	173.00
Isobutyl methacrylate monomer	103.86
"Solvesso" 100	45.02
<u>Portion III</u>	
2,2-(2-methyl butane nitrile)	57.32
"Solvesso" 100	<u>85.80</u>
Total	840.00



The "Solvesso" 100 is a conventional aromatic hydrocarbon solvent. Portion I is charged into the reactor and heated to its reflux temperature. Portion II, containing the monomers for the organosilane polymer, and Portion III, containing the polymerization initiator, are each premixed and then added simultaneously to the reactor while the reaction mixture is held at its reflux temperature. Portion II is added at a uniform rate over a 6 hour period and Portion II is added at a uniform rate over a 7 hour period. After Portion II is added, the reaction mixture is held at its reflux temperature for an additional hour. The resulting acrylosilane polymer solution is cooled at room temperature and filtered.

The resulting acrylosilane polymer solution has a polymer solids content of about 70%, the polymer has a weight average molecular weight of about 3,000, and has the following constituents: 30% styrene, 18% isobutyl methacrylate, and 52% methacryloxypropyl trimethoxysilane.

15

### EXAMPLE 3

This example illustrates an epoxy-silane polymer, more particularly an epoxy functional acrylosilane polymer which was prepared by charging the following constituents into a polymerization vessel equipped with a heating mantle, reflux condenser, thermometer, nitrogen inlet, and stirrer:

	<u>Portion 1</u>	<u>Parts by Weight</u>
	Xylol (135-145°C)	363.2
25	Aromatic 100	363.2
	<u>Portion 2</u>	
	Styrene	530.9
	gamma-Methacryloxypropyl trimethoxy silane	1380.3
30	Methyl methacrylate	318.5
	Butyl methacrylate	79.6
	2-Ethylhexyl acrylate	79.6
	Glycidyl methacrylate	265.4
	Aromatic 100	40.9
35	Xylol	40.9

	<u>Portion 3</u>	
	t-Butyl peroxyacetate	132.7
	Aromatic 100	99.6
5	Xylol	<u>99.7</u>
	TOTAL	3794.5

10 Portion 1 was charged into the polymerization vessel and heated under nitrogen to 149°C. Portion 2 was then added over 360 minutes and Portion 3 over 420 minutes to the vessel. The resulting polymer solution had the following characteristics:

	Gallon wt.	8.56 lbs./gal.
15	% wt. solids	72.2%
	% volume solids	68.6
	M <sub>w</sub> of polymer	5000
	M <sub>n</sub> of polymer	1650

20 The polymer composition was, by weight, 20 percent styrene, 52 percent gamma-methacryloxypropyl trimethoxy silane (A-174 commercially available from Union Carbide, Inc., Danbury, Conn.), 12 percent methyl methacrylate, 3 percent butyl methacrylate, 3 percent 2-ethylhexyl acrylate, and 10 percent glycidyl methacrylate, represented as  
 25 follows: STY/A-174/MMA/BMA/2-EHA/GMA in the ratio of 20 / 52 / 12 / 3 / 3 / 10.

#### EXAMPLE 4

30 This example illustrates, as an optional component for a composition according to the present invention, a polyester urethane solution which may be prepared by charging the following constituents in order into a reaction vessel equipped with a stirrer, a heating source and a reflux condenser:

	<u>Portion 1</u>	<u>Parts by Weight</u>
	1,3-butylene glycol	173.4
	1,6-hexanediol	163.1
5	Trimethylol propane	78.8
	Adipic acid	403.7
	Toluene	20.0
	<u>Portion 2</u>	
	Propylene glycol monomethyl ether acetate	294.4
10	<u>Portion 3</u>	
	Tone® FCP 310 (caprolactone polyol from Union Carbide)	934.9
	Propylene glycol monomethyl ether acetate	185.3
	Hydrocarbon solvent	706.1
15	<u>Portion 4</u>	
	trimethylhexamethylene diisocyanate	290.3
	dibutyl tin dilaurate	0.5
	<u>Portion 5</u>	
	Hydrocarbon solvent	<u>69.8</u>
20	Total	3320.3

Portion 1 is charged in order into the reaction vessel, and the constituents of Portion 1 are heated to distill water at 140-230°C. The distillation is continued until the acid number is 6.5 to 8.5. The product is thinned and cooled to 98° to 102°C by charging Portion 2 into the vessel. While the constituents in the vessel are maintained at the above temperature, Portion 3 was charged to the reactor in order. Portion 4 is added to the composition at a uniform rate over a 30 minute period while the batch temperature is maintained at 98°-102°C. A sample is removed and tested for unreacted isocyanate NCO by infrared analysis. The composition is held at the above temperature until there is no unreacted isocyanate in the composition. Portion 5 then is added as a rinse and the resulting composition was allowed to cool to ambient temperatures.

Following this procedure, the resulting composition had a polymer weight solids content of about 61.0%. The polyester urethane had a Gardner-Holdt viscosity of L. The  $M_n$  (number average molecular weight) was 3734.0 and the  $M_w$  (weight average molecular weight) was 7818.0 (by gel permeation chromatography using polystyrene as the standard). The acid content was determined to be 4.9 Meq/g. The hydroxy number was 92.

#### EXAMPLE 5

This example illustrates a clearcoat coating composition according to the present invention. The following was thoroughly blended:

<u>Components</u>	<u>Parts</u>
Acid Resin (prepared as described above)	35.1
Propylene glycol monomethyl ether acetate	27.28
DISLON 1984 acrylic flow additive (50%) in xylene, from King Industries	0.17
XU-71950 (diglycidylester from Dow)	10.04
Catalyst solution	5.92
CYMEL 325 (Melamine)	4.76
Epoxy-silane polymer (prepared as described above)	10.92
TINUVIN 384 (UV Screener from Ciba-Geigy)	0.72
TINUVIN 123 (HALS from Ciba-Geigy)	0.53
Trimethyl orthoacetate	<u>4.56</u>
TOTAL	100.00

In the above list, fully capitalized names indicate trademarks of commercially available products. The UV screener and hindered amine light stabilizer (HALS) are commercially available from Ciba-Geigy as indicated above. The catalyst solution refers to a solution of benzyl triphenyl phosphonium chloride, which may be prepared from a mixture of 62.8 parts of ethylene glycol-MHHPA half-ester, 29.9 parts of xylene, and 7.3 parts of benzyl triphenyl phosphonium chloride, in which the solution was heated to 50-60°C to dissolve the phosphonium chloride catalyst. The MHHPA half-ester was prepared as follows: 578.7 parts of methyl hexahydrophthalic anhydride and 249.7 parts of xylene were heated to 160°F and 106.2 parts of

ethylene glycol were added over 45 minutes. After the feed was complete, the reaction was maintained at 250 +/-10 °F for 5 hours to complete the reaction. Finally, the reaction product was cooled to 150 °F and 8.8 parts of methanol was added. The mixture was stirred for 60 minutes and heated to  
5 reflux to remove solvent, cooled to 160 °F, and filtered (75 weight percent solids).

The coating composition was sprayed onto primed metal panels coated with a basecoat and cured at 265°F. The coating exhibited excellent humidity resistance, chemical resistance, durability and other film  
10 properties.

Various modifications, alterations, additions, or substitutions of the components of the composition of this invention will be apparent to those skilled in the art without departing from the scope and spirit of this  
15 invention. This invention is not limited to the illustrative embodiments set forth herein, but rather the invention is defined by the following claims.

## WE CLAIM:

- 5 1. A coating composition comprising 20-80% by weight of reactive binder components and 80-20% by weight of an organic liquid carrier; wherein the binder comprises:
- 10 (a) 25-90% by weight, based on the weight of the binder, of an acrylic copolymer having at least two reactive acid groups and comprising polymerized monomers of an ethylenically unsaturated acid or an ethylenically unsaturated dicarboxylic acid and polymerized monomers selected from the group consisting of alkyl methacrylate, alkyl acrylate and any mixtures thereof, wherein the alkyl groups have 1-8 carbon atoms and the polymer has a weight average molecular weight of about 2,000-50,000;
- 15 (b) 5-30% by weight, based on the weight of the binder, of a glycidyl component having at least two reactive glycidyl groups;
- (c) 5-30% by weight, based on the weight of the binder, of a polymeric melamine resin;
- 20 (d) 5-30% by weight, based on the weight of the binder, of a polymer having silane groups; and
- (e) an effective amount of a curing catalyst.
- 25 2. The coating composition of claim 1, wherein the glycidyl component comprises a di- or polyglycidyl ester of a polyol or a di- or polyglycidyl ester of a carboxylic acid.
- 30 3. The coating composition of claim 1 in which the glycidyl component is selected from the group consisting of a polyglycidyl ether of low molecular weight polyol, an epoxy resin of epichlorohydrin and bisphenol A, a polyglycidyl ester of a polycarboxylic acid, a polyglycidyl ether of isocyanurate, a glycidyl methacrylate or glycidyl acrylate containing acrylic polymer, and compatible mixtures of any of the above.

4. The coating composition of claim 1, further comprising a polyester urethane polyol.

5. The coating composition of claim 1, in which the acid acrylic polymer comprises polymerized monomers of styrene, alkyl methacrylate or an alkyl acrylate having 2-4 carbon atoms in the alkyl group, and ethylenically unsaturated acid or ethylenically unsaturated dicarboxylic acid.

6. The coating composition of claim 1, in which the acid acrylic polymer consists of polymerized monomers of maleic acid or itaconic acid.

7. The coating composition of claim 1, wherein component (d) is an epoxy-functional acrylosilane polymer.

8. The composition of claim 1, further comprising an effective amount of an alkyl orthoacetate.

9. The coating composition of claim 4, in which the polyester urethane has a hydroxyl number of about 20-120 or an acid number of 20 to 120.

10. The coating composition of claim 1, wherein the catalyst is a phosphonium compound.

11. The coating composition of claim 1, further comprising a half ester which is the reaction product of an alcohol or glycol and a monomeric anhydride of a dicarboxylic acid.

12. The coating composition of claim 11, wherein the half ester is the reaction of an alcohol or glycol and methylhexahydrophthalic anhydride.

13. The coating composition of claim 1 containing about 0.1-200% by weight, based on the weight of the binder, of pigment.

14. A substrate coated with a cured layer of the composition of claim 1.

5      15. The substrate of claim 14, wherein said substrate is plastic or metal.



**AMENDED CLAIMS**

[received by the International Bureau on 21 April 1994 (21.04.94);  
original claims 10-15 cancelled; original claim 1 amended;  
other claims unchanged (2 pages)]

1. A clearcoat composition which is essentially anhydride-free comprising 20-80% by weight of reactive binder components and 80-20% by weight of an organic liquid carrier; wherein the binder comprises:

- (a) 25-90% by weight, based on the weight of the binder, of an acrylic copolymer having at least two reactive acid groups and comprising polymerized monomers of an ethylenically unsaturated monoacid or an ethylenically unsaturated dicarboxylic acid and polymerized monomers selected from the group consisting of alkyl methacrylate, alkyl acrylate and any mixtures thereof, wherein the alkyl groups have 1-8 carbon atoms and the polymer has a weight average molecular weight of about 2,000-50,000;
- (b) 5-30% by weight, based on the weight of the binder, of a glycidyl ether or ester or cycloaliphatic epoxy compound containing at least two reactive glycidyl groups;
- (c) 5-30% by weight, based on the weight of the binder, of an alkylated melamine formaldehyde resin that is partially or fully alkylated and has a degree of polymerization of about 1 to 5; and
- (d) 10-30% by weight, based on the weight of the binder, of an acylosilane polymer which is the polymerization product of about 5-70% by weight ethylenically unsaturated alkoxy silane containing monomers, based on the weight of the polymer, and having a number average molecular weight of 500-10,000; and
- (e) an effective amount of a curing catalyst selected from the group consisting of tertiary amines, quaternary ammonium salts, and phosphonium compounds;

wherein components (a), (b), (c), and (d) are different components.

2. The coating composition of claim 1, wherein the glycidyl component comprises a di- or polyglycidyl ether of a polyol or a di- or polyglycidyl ester of a di- or polycarboxylic acid.

3. The coating composition of claim 1 in which the glycidyl component is selected from the group consisting of a polyglycidyl ether of low

molecular weight polyol, an epoxy resin of epichlorohydrin and bisphenol A, a polyglycidyl ester of a polycarboxylic acid, a polyglycidyl ether of isocyanurate, a glycidyl methacrylate or glycidyl acrylate containing acrylic polymer, and mixtures of any of the above.

4. The coating composition of claim 1, in which the acid acrylic polymer comprises polymerized monomers of styrene, alkyl methacrylate or an alkyl acrylate having 2-4 carbon atoms in the alkyl group, and ethylenically unsaturated acid or ethylenically unsaturated dicarboxylic acid.

5. The coating composition of claim 1, in which the acid acrylic polymer consists of polymerized monomers of maleic acid or itaconic acid.

6. The coating composition of claim 1, wherein component (d) is an epoxy-functional acrylosilane polymer.

7. The composition of claim 1, further comprising an effective amount of an alkyl orthoacetate.

8. The coating composition of claim 1, wherein the catalyst is a phosphonium compound.

9. A substrate coated with a cured layer of the composition of claim 1.

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/10792

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(5) : Please See Extra Sheet. US CL : 523/429, 433, 455; 525/101 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 523/429, 433, 435, 455; 525/101 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,681,811 (SIMPSON et al) 21 JULY 1987, col. 1, line 63 to col. 2, line 9, col. 2, lines 16-19, col. 5, lines 53-50, col. 10, lines 20-30, and col. 10, lines 31-44.	1-3, 5-8, 10, 13-15
Y	US, A, 5,069,767 (TOMINAGA) 03 DECEMBER 1991, col. 4, lines 23-29, col. 5, lines 43-59 and col. 8, lines 14-18.	1-3, 5-8, 10, 13-15
Y	US, A, 5,162,426 (HAZAN et al) 10 NOVEMBER 1992, col. 4, lines 18-61, and col. 5, lines 34-47.	1-3, 5-8, 10, 13-15
Y	US, A, 4,975,488 (FURUKAWA et al) 04 DECEMBER 1990, col. 3, lines 31-32 and col. 9, lines 53-68.	1-3, 5-8, 10, 13-15
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: *A* document defining the general state of the art which is not considered to be part of particular relevance *E* earlier document published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art *&* document member of the same patent family	
Date of the actual completion of the international search 15 FEBRUARY 1994		Date of mailing of the international search report <b>MAR 14 1994</b>
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE		Authorized officer <i>Renew Leavel for</i> DONALD R. WILSON Telephone No. (703) 305-2351

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/10792

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,871,806 (SHALATI et al) 03 OCTOBER 1989, col. 10, lines 64-68.	10
Y	US, A, 5,039,385 (TOMINAGA) 13 AUGUST 1991, col. 4, lines 35-55 and col. 6, lines 26-44.	1-3, 5-8, 10, 13-15

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/10792**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:  
1-3, 5-8, 10 and 13-15

Remark on Protest

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/10792

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (5):

C08K 5/01, 5/06, 5/11; C08L 31/02, 43/04, 61/28, 63/00; C09D 133/06, 143/04, 161/28, 163/00

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

I. Claims 1-3, 5-8, 10 and 13-15 drawn to an epoxy/melamine/acid/ acrylic polymer coating composition, classified in Class 523, subclass 435.

II. Claims 4 and 9, drawn to an epoxy/melamine/urethane/acid acrylic polymer coating composition, classified in Class 523, subclass 435.

III. Claims 11 and 12, drawn to epoxy/melamine/acid acrylic polymer with reactive diluent coating composition, classified in Class 523, subclass 435.