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(54) **COMPOSITION DE REVETEMENT RESISTANT A L'ABRASION**

(54) **MAR RESISTANT COATING COMPOSITION**

(57) Une composition filmogène résistante aux rayures et à l'attaque chimique contient un polyépoxyde qui est sensiblement exempt de groupes silyle, un agent durcissant du type polyacide et un additif en une quantité suffisante pour améliorer la résistance aux rayures. Cet additif est une solution d'un polymère d'un monomère insaturé d'éthylène et d'un monomère polymérisable du type alcoxysilane. La composition filmogène est particulièrement avantageuse pour réaliser une couche de finition transparente sur une couche de base colorée dans un système de revêtement couleur + couche transparente, destiné aux automobiles.

(57) A mar and etch resistant film forming composition contains a polyepoxide which is essentially free of silyl moieties, a polyacid curing agent and an additive amount effective to improve mar resistance of a solution polymer of an ethylenically unsaturated monomer component containing a polymerizable alkoxy silane monomer. The film forming composition is particularly advantageous as a clear topcoat over a pigmented basecoat in a color-plus-clear automotive coating system.

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(54) Title: MAR RESISTANT COATING COMPOSITION

(57) Abstract

A mar and etch resistant film forming composition contains a polyepoxide which is essentially free of silyl moieties, a polyacid curing agent and an additive amount effective to improve mar resistance of a solution polymer of an ethylenically unsaturated monomer component containing a polymerizable alkoxy silane monomer. The film forming composition is particularly advantageous as a clear topcoat over a pigmented basecoat in a color-plus-clear automotive coating system.

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MAR RESISTANT COATING COMPOSITION

BACKGROUND OF THE INVENTION

The present invention relates to coating compositions based on polyepoxides cured with polyacids and on the use of compositions in color-plus-clear coating systems.

Original equipment finish coating systems for automobiles have utilized color-plus-clear technology for a number of years. This technology involves the application of a pigmented or otherwise colored base coat to a substrate, followed by the application of a transparent or clear topcoat to the basecoat. The clearcoat imparts high gloss and distinctness of image to the system as well as protecting the basecoat from environmental attack.

In more recent years, such original equipment finish coatings have been required to demonstrate resistance to etching of the finished surface by atmospheric acid precipitation, otherwise referred to as acid-etch resistance. To address this requirement, original equipment finish coating systems based on polyepoxides cured with polyacids have been developed which meet or exceed the acid-etch resistance requirements of automotive manufacturers.

In addition to the requirement of acid-etch resistance, original equipment finish coatings must also demonstrate resistance to mar and scratching. The polyepoxide polyacid based coating systems, while possessing good acid-etch resistance, have not provided adequate mar resistance. While microparticulate materials such as silica, metal sulfides, or crosslinked styrene-butadiene have been added to such coatings, to improve mar resistance, these materials typically adversely affect gloss and distinctness of image (DOI) of the coating due to the scattering of light at the particle interfaces. Thus their effectiveness has been limited. It would be thus desirable to have an original equipment finish automotive color-plus-clear polyepoxide polyacid based coating system which could provide good mar resistance while maintaining excellent acid-etch resistance, gloss and DOI.

SUMMARY OF THE INVENTION

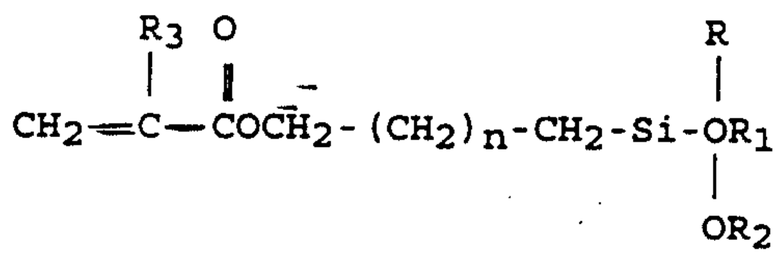
In accordance with the present invention, there is provided a mar and acid-etch resistant film forming composition, comprising a polyepoxide which is essentially free of silyl moieties, a polyacid curing agent, and an additive amount effective to improve mar resistance of a solution polymer of an ethylenically unsaturated monomer component comprising a polymerizable alkoxy silane monomer.

Also provided in accordance with the present invention is a method of applying a coating composition to a substrate comprising applying to the substrate a pigmented film-forming composition to form a basecoat and applying to said basecoat as a topcoat a clear mar and acid-etch resistant film-forming composition according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

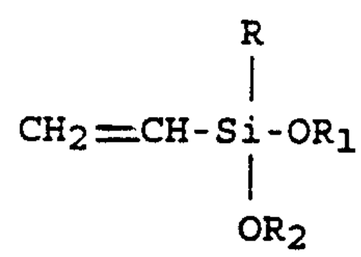
The film forming composition of the present invention is based on a polyepoxide polymer and a polyacid curing agent. The polyepoxide polymer is essentially free of silyl moieties; that is the polyepoxide polymer contains no more than about 1 percent, preferably no more than about 0.1 percent of silicon, the percentage based on the total weight of the polyepoxide polymer. The film forming composition also contains a solution polymer synthesized from an ethylenically unsaturated monomer component comprising a polymerizable ethylenically unsaturated alkoxy silane monomer. Preferably the ethylenically unsaturated monomer component additionally contains at least one other polymerizable ethylenically unsaturated monomer. The claimed film forming compositions are particularly advantageous in exhibiting improved mar resistance in conjunction with good acid etch resistance and overall appearance of the cured film.

The amount of polymerizable alkoxy silane monomer present in the monomer component ranges from about 60 to about 100, preferably from about 60 to about 80 percent by weight, the percentages based on total weight of the monomers present in the monomer component. Suitable polymerizable alkoxy silane monomers include those represented by the following structures I and II:



(I)

where R is CH_3, CH_3CH_2, CH_3O, or CH_3CH_2O; R_1 and R_2 independently are CH_3 or CH_3CH_2; R_3 is H, CH_3, or CH_3CH_2; and n is 0 or a positive integer from 1 to 10. Preferably, R is CH_3O or CH_3CH_2O and n is 1.



(II)

where R, R_1 and R_2 are as described above.

Typical examples of alkoxy silane monomers with structure (I) include acrylatoalkoxy silanes, such as gamma-acryloxypropyltrimethoxy silane, and the methacrylatoalkoxy silanes, such as gamma-methacryloxypropyltrimethoxy silane and gamma-methacryloxypropyltris(2-methoxyethoxy)silane.

Examples of alkoxy silane monomers with structure (II) are the vinylalkoxy silanes, such as vinyl trimethoxy silane, vinyl triethoxy silane and vinyl tris(2-methoxyethoxy)silane.

Further suitable alkoxy silane monomers include ethylenically unsaturated acryloxysilanes, such as acrylatoxy silane and methacrylatoxy silane, vinylacetoxy silanes, such as vinylmethyl

diacetoxy silane, acrylatopropyltriacetoxy silane, and methacrylatopropyltriacetoxy silane, or any mixture of the above alkoxy silane monomers. Preferably the alkoxy silane monomer is gamma-methacryloxypropyltrimethoxysilane.

The other polymerizable ethylenically unsaturated monomer is present in the ethylenically unsaturated monomer component in an amount generally ranging from about 0 to about 40 percent, preferably from about 20 to about 40 percent by weight, the percentages based on the total weight of the monomers present in the ethylenically unsaturated monomer component. Examples of suitable polymerizable ethylenically unsaturated monomers include alkylacrylates and alkylmethacrylates having from 1 to 20 carbon atoms in the alkyl group such as methyl acrylate, methyl methacrylate, ethyl acrylate, n-butyl acrylate, n-butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate; vinyl aromatic monomers such as styrene, alpha-methyl styrene, and vinyl toluene; nitrile monomers such as acrylonitrile and methacrylonitrile. Preferably the other ethylenically unsaturated monomer is n-butyl methacrylate.

The solution polymer is synthesized utilizing standard free radical initiated solution polymerization techniques well known to those skilled in the art of polymer chemistry. Generally the polymerization is conducted in a high boiling solvent such as Solvesso®-100 (aromatic hydrocarbon, commercially available from Exxon Chemical Company) under nitrogen or similar inert atmosphere to maintain a moisture free environment. The polymerization is generally conducted at reflux temperature for a period ranging from about 1 to 10 hours, preferably from about 5 to 8 hours. Suitable free radical initiators include organic peroxides such as di-tert-butylperoxide, benzoyl peroxide, and dicumene peroxide; and azo compounds such as 2,2'-azobis(2-methylbutane nitrile). The amount of free radical initiator can vary depending upon the particular reaction conditions but typically from about 3 percent to about 8 percent, based on total weight of the monomers present, is used. The reaction is considered complete when the total free monomer

concentration is less than about 2 percent by weight, the percentage based on the total weight of the reaction mixture.

The solution polymer is used in the film forming composition in an amount effective to improve mar resistance while maintaining acid-etch resistance, gloss and DOI. Typically, the amount will vary from about 1 to about 20 percent, preferably from about 10 to about 20 percent by weight, the percentage based on the total weight of the resin solids of the composition. The solution polymer generally has a number average molecular weight ranging from about 500 to about 20,000, preferably from about 1200 to about 5000, as determined by gel permeation chromatography (GPC) using polystyrene standards.

The mar and acid-etch resistant film forming composition which contains the solution polymer is preferably a clear film forming composition which is used to form a transparent topcoat over a pigmented basecoat. As mentioned above, the clear film-forming composition according to the present invention comprises as a film former a polyepoxide resin which is essentially free of silyl moieties and a polyacid curing agent which preferably comprises a half-ester formed from reacting an acid anhydride with a polyol.

The polyepoxides which can be used include epoxy-containing acrylic polymers, epoxy condensation polymers such as polyglycidyl ethers of alcohols and phenols, polyglycidyl esters of polycarboxylic acids, and mixtures of the foregoing. By essentially free of silyl moieties is meant that the polyepoxide polymer contains no more than about 1 percent silicon, preferably less than about 0.1 percent silicon, the percentage based on the total weight of the polyepoxide polymer.

A suitable epoxy-containing acrylic polymer is a copolymer of an ethylenically unsaturated monomer having at least one epoxy group and at least one polymerizable ethylenically unsaturated monomer which is free of epoxy groups.

Examples of ethylenically unsaturated monomers containing epoxy groups are those containing 1,2-epoxy groups and include glycidyl acrylate, glycidyl methacrylate and allyl glycidyl ether.

Examples of ethylenically unsaturated monomers which do not contain epoxy groups are alkyl esters of acrylic and methacrylic acid containing from 1 to 20 carbon atoms in the alkyl group. Specific examples of these acrylates and methacrylates include methyl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, ethyl acrylate, n-butyl acrylate and 2-ethylhexyl acrylate. Examples of other copolymerizable ethylenically unsaturated monomers are vinyl aromatic compounds such as styrene, alpha-methyl styrene, and vinyl toluene; nitriles such as acrylonitrile and methacrylonitrile; vinyl and vinylidene halides such as vinyl chloride and vinylidene fluoride and vinyl esters such as vinyl acetate.

The epoxy group-containing ethylenically unsaturated monomer is preferably used in amounts of from about 5 to about 90, more preferably from about 20 to about 70 percent by weight of the total monomers used in preparing the epoxy-containing acrylic polymer. Of the remaining polymerizable ethylenically unsaturated monomers, preferably from about 10 to about 95 percent, more preferably from about 30 to about 80 percent by weight of the total monomers are the alkyl esters of acrylic and methacrylic acid.

The epoxy containing acrylic polymer can be prepared by well known free radical initiated solution polymerization techniques in the presence of suitable free radical initiators such as organic peroxides, such as t-butyl perbenzoate, t-amyl peracetate or ethyl-3,3-di(t-amylperoxy)butyrate or azo compounds, such as 2,2'-azobis(2-methylbutane nitrile) and 2,2'-azobis(2-methylpropane nitrile). The polymerization is typically carried out in an organic solvent in which the monomers and the polymer are soluble. Suitable solvents are aromatic solvents such as xylene and toluene, ketones such as

methyl amyl ketone or ester solvents such as ethyl 3-ethoxypropionate.

Suitable epoxy condensation polymers include polyepoxides having a 1,2-epoxy equivalency greater than 1, preferably greater than 1 and up to about 5.0. Useful examples of such polyepoxides are polyglycidyl esters from the reaction of polycarboxylic acids with epihalohydrins such as epichlorohydrin. The polycarboxylic acid can be formed by any method known in the art and in particular, by the reaction of aliphatic alcohols with an anhydride, and in particular, diols and higher functionality alcohols. For example, trimethylol propane or pentaerythritol can be reacted with hexahydrophthalic anhydride to produce a polycarboxylic acid which is then reacted with epichlorohydrin to produce a polyglycidyl ester. Additionally, the polycarboxylic acid can be an acid-functional acrylic polymer.

Further examples of such epoxides are polyglycidyl ethers of polyhydric phenols and of aliphatic alcohols. These polyepoxides can be produced by etherification of the polyhydric phenol or aliphatic alcohol with an epihalohydrin such as epichlorohydrin in the presence of alkali.

Examples of suitable polyhydric phenols are 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) and 1,1-bis(4-hydroxyphenyl)ethane. Examples of suitable aliphatic alcohols are ethylene glycol, diethylene glycol, pentaerythritol, trimethylol propane, 1,2-propylene glycol and 1,4-butylene glycol. Also, cycloaliphatic polyols such as 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,4 cyclohexane dimethanol, 1,2-bis(hydroxymethyl)cyclohexane and hydrogenated bisphenol A can also be used.

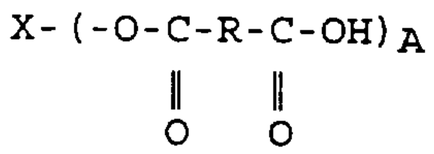
Besides the polyepoxides described above, certain polyepoxide monomers and oligomers can also be used. Examples of these materials are described in U.S. Patent No. 4,102,942 in column 3, lines 1-16. Specific examples of such low molecular weight polyepoxides are 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate and bis(3,4-epoxycyclohexylmethyl) adipate. These materials are aliphatic polyepoxides as are the epoxy-containing acrylic polymers described above. As mentioned above, the epoxy-containing acrylic polymers are preferred because they result in products which have the optimum combination of coating properties, i.e., smoothness, gloss, durability and solvent resistance. Such polymers have been found to be particularly useful in the formulation of clear coats for color-plus-clear applications. Of course, as mentioned above, mixtures of these polyepoxides can be used.

The polyepoxide is present in the film-forming composition in amounts of from about 10 percent by weight to about 90 percent by weight, preferably from about 20 percent by weight to about 80 percent by weight and more preferably from about 40 percent by weight to about 70 percent by weight, the percentage based on total weight of resin solids.

The polyacid curing agent contains two or more acid groups per molecule which are reactive with the polyepoxide to form a crosslinked coating film as indicated by the film's resistance to organic solvent. The polyacid curing agent preferably comprises a half-ester formed from reacting an acid anhydride with a polyol. The acid functionality is preferably carboxylic acid, although acids such as sulfonic acid may be used but their use is not preferred. The half-esters are relatively low in molecular weight and quite reactive with epoxies enabling the formation of high solids fluid compositions while maintaining outstanding properties such as gloss and distinctness of image.

The half-ester is obtained by reaction between a polyol and a 1,2-acid anhydride under conditions sufficient to open the anhydride ring forming the half-ester with substantially no polyesterification occurring. Such reaction products are of relatively low molecular weight with narrow molecular weight distributions and low viscosity and provide lower volatile organic contents in the coating composition while still providing for excellent properties in the resultant coating. By substantially no polyesterification occurring means that the carboxyl groups formed by the reaction of the anhydride are not further esterified by the polyol in a recurring manner. By this is meant that less than about 10, preferably less than about 5 percent by weight high molecular weight polyester is formed.

Two reactions may occur in combining the anhydride and the polyol together under suitable reaction conditions. The desired reaction mode involves ring opening the anhydride ring with hydroxyl, i.e.,



where X is the residue of the polyol after the polyol has been reacted with a 1,2-dicarboxylic acid anhydride, R is an organic moiety from the anhydride and A is an integer equal to at least 2.

Subsequently, carboxylic acid groups formed by opening of the anhydride ring may react with hydroxyl groups to give off water via a condensation reaction. This latter reaction is not desired since it can lead to a polycondensation reaction resulting in products with higher molecular weights.

To achieve the desired reaction, the 1,2-acid anhydride and polyol are contacted together usually by mixing the two ingredients together in a reaction vessel, preferably in the presence of an inert atmosphere such as nitrogen and in the presence of a solvent to dissolve the solid ingredients and/or to lower the viscosity of the reaction mixture. Examples of suitable solvents are high boiling materials and include, for example, ketones such as

methyl amyl ketone, diisobutyl ketone, methyl isobutyl ketone; aromatic hydrocarbons such as toluene and xylene; as well as other organic solvents such as dimethyl formamide and N-methyl-pyrrolidone.

For the desired ring opening reaction and half-ester formation, a 1,2-dicarboxylic anhydride is used. Reaction of a polyol with a carboxylic acid instead of an anhydride would require esterification by condensation with elimination of water which would have to be removed by distillation. Under these conditions this would promote undesired polyesterification. Also, the reaction temperature is preferably low, that is, no greater than about 135°C, preferably less than about 120°C, and usually within the range of about 70° to about 135°C, preferably about 90° to about 120°C. Temperatures greater than 135°C are undesirable because they promote polyesterification, whereas temperatures less than 70°C are undesirable because of sluggish reaction rates.

The time of reaction can vary somewhat depending principally upon the temperature of reaction. Usually the reaction time will vary from about 10 minutes to about 24 hours.

The equivalent ratio of anhydride to hydroxyl on the polyol is preferably at least about 0.8:1 (the anhydride being considered monofunctional) to obtain maximum conversion to the desired half-ester. Ratios less than 0.8:1 can be used but such ratios result in increased formation of lower functionality half-esters.

Among the anhydrides which can be used in formation of the desired polyesters are those which, exclusive of the carbon atoms on the anhydride moiety, contain from about 2 to 30 carbon atoms. Examples include aliphatic, including cycloaliphatic, olefinic and cycloolefinic anhydrides and aromatic anhydrides. Substituted aliphatic and aromatic anhydrides are also included within the definition of aliphatic and aromatic provided the substituents do not adversely affect the reactivity of the anhydride or the properties of the resultant polyester. Examples of substituents would be chloro, alkyl and alkoxy. Examples of anhydrides include succinic anhydride, methylsuccinic anhydride, dodecenyl succinic anhydride, octadecenylsuccinic anhydride, phthalic anhydride, tetrahydrophthalic

anhydride, methyltetrahydrophthalic anhydride, hexahydrophthalic anhydride, alkyl hexahydrophthalic anhydrides such as methylhexahydrophthalic anhydride, tetrachlorophthalic anhydride, endomethylene tetrahydrophthalic anhydride, chlorendic anhydride, itaconic anhydride, citraconic anhydride and maleic anhydride.

Among the polyols which can be used are simple polyols, that is, those containing from about 2 to 20 carbon atoms, as well as oligomeric polyols and polymeric polyols such as polyester polyols, polyurethane polyols and acrylic polyols.

Among the simple polyols are diols, triols, tetrols and mixtures thereof. Examples of the polyols are preferably those containing from 2 to 10 carbon atoms such as aliphatic polyols. Specific examples include but are not limited to the following compositions: di-trimethylol propane(bis(2,2-dimethylol)dibutylether); pentaerythritol; 1,2,3,4-butanetetrol; sorbitol; trimethylol propane (TMP); trimethylol ethane; 1,2,6-hexanetriol; 1,3,6-hexanetriol; glycerine; trishydroxyethyl isocyanurate; dimethylol propionic acid; 1,2,4-butanetriol; 1,3,4-butanetriol; TMP/epsilon-caprolactone triols; ethylene glycol; 1,2-propanediol; 1,3-propanediol; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; neopentyl glycol; diethylene glycol; dipropylene glycol; 1,4-cyclohexanedimethanol and 2,2,4-trimethylpentane-1,3 diol.

Suitable oligomeric polyols, include polyols made from reaction of diacids with triols, such as trimethylol propane/cyclohexane diacid and trimethylol propane/adipic acid.

With regard to polymeric polyols, the polyester polyols are prepared by esterification of an organic polycarboxylic acid or anhydride thereof with organic polyols and/or an epoxide. Usually, the polycarboxylic acids and polyols are aliphatic or aromatic dibasic acids or acid anhydrides and diols.

The polyols which are usually employed in making the polyester include trimethylol propane, di-trimethylol propane, alkylene glycols such as ethylene glycol, neopentyl glycol and other glycols such as hydrogenated bisphenol A, cyclohexanediol, cyclohexanedimethanol, the reaction products of lactones and diols, for example, the reaction product of epsilon-caprolactone and ethylene glycol, hydroxy-alkylated bisphenols, polyester glycols, for example, poly(oxytetramethylene)glycol and the like.

The acid component of the polyester consists primarily of monomeric carboxylic acids or anhydrides having 2 to 18 carbon atoms per molecule. Among the acids which are useful are phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, methylhexahydrophthalic acid, adipic acid, azelaic acid, sebacic acid, maleic acid, glutaric acid, chlorendic acid, tetrachlorophthalic acid and other dicarboxylic acids of varying types. Also, there may be employed higher polycarboxylic acids such as trimellitic acid and tricarballylic acid. However, the use of these higher functionality polycarboxylic acids are not preferred because of resultant high viscosities.

Besides the polyester polyols formed from polybasic acids and polyols, polylactone-type polyesters can also be employed. These products are formed from the reaction of a lactone such as epsilon-caprolactone and a polyol such as ethylene glycol, diethylene glycol and trimethylolpropane.

Besides polyester polyols, polyurethane polyols such as polyester-urethane polyols which are formed from reacting an organic polyisocyanate with a polyester polyol such as those described above can be used. The organic polyisocyanate is reacted with a polyol so that the OH/NCO equivalent ratio is greater than 1:1 so that the resultant product contains free hydroxyl groups. The organic polyisocyanate which is used in preparing the polyurethane polyols

can be an aliphatic or aromatic polyisocyanate or a mixture. Diisocyanates are preferred, although higher polyisocyanates such as triisocyanates can be used, but they do result in higher viscosities.

Examples of suitable diisocyanates are 4,4'-diphenylmethane diisocyanate, 1,4-tetramethylene diisocyanate, isophorone diisocyanate and 4,4'-methylenebis(cyclohexyl isocyanate). Examples of suitable higher functionality polyisocyanates are polymethylene polyphenol isocyanates.

It is also possible to use as the polyacid curing agent acid-functional acrylic crosslinkers made from copolymerizing methacrylic acid and/or acrylic acid monomers with other ethylenically unsaturated copolymerizable monomers. Alternatively, acid-functional acrylic crosslinkers can be prepared from hydroxy-functional acrylic monomers reacted with cyclic anhydrides.

The polyacid curing agent is present in the film forming composition in amounts of from about 10 to about 90, preferably about 25 to about 75 percent by weight, the percentages based on total weight of resin solids.

Optional film forming materials which are preferably added to the claimed compositions include an acid functional acrylic polymer and an anhydride.

The acid functional acrylic polymers are reaction products of an ethylenically unsaturated polymerizable carboxylic acid such as acrylic acid or methacrylic acid with another ethylenically unsaturated polymerizable monomer different from said acids. These products are non-gelled and typically will have number average molecular weights as determined by gel permeation chromatography, using polystyrene standards, of from about 500 to about 5000, preferably about 700 to about 3000.

The amount of acid functional acrylic polymer which is used can vary from 0 to about 50, preferably from about 10 to about 20 percent by weight based on total weight of resin solids.

The polyepoxide-polyacid compositions also preferably contain an anhydride, preferably an anhydride which is a liquid at 25 °C. The presence of such an anhydride in the compositions provides an improved cure response. Examples of suitable anhydrides include alkyl-substituted hexahydrophthalic anhydrides such as methyl hexahydrophthalic anhydride and dodecenyl succinic anhydride. The amount of the anhydride which is used can vary from 0 to about 40, preferably from about 5 to about 25 percent by weight based on total weight of resin solids.

The equivalent ratio of carboxylic acid in the polyacid curing agent to epoxy in the polyepoxide in the clear film-forming compositions can vary depending upon the particular curing conditions. For example, at higher temperatures a lower equivalent ratio can be used whereas at lower temperatures a higher equivalent ratio is more suitable. Preferably the ratio is adjusted so that there are about 0.3 to about 3.0, preferably about 0.8 to about 1.5 equivalents of carboxyl (anhydride being considered monofunctional) per equivalent of epoxy, that is the equivalent ratio of acid to epoxy ranges from about 0.3:1 to about 3.0:1, preferably from about 0.8:1 to about 1.5:1.

The compositions will also preferably contain catalysts to accelerate the cure of the epoxy and acid groups. Examples of suitable catalysts include organic amines and quaternary ammonium compounds such as pyridine, piperidine, dimethylaniline, diethylenetriamine, tetramethylammonium chloride, tetramethylammonium acetate, tetramethylbenzylammonium acetate, tetrabutylammonium fluoride, and tetrabutylammonium bromide. The amount of catalyst typically ranges from 0 to about 10 percent, preferably from about 0.5 to about 3 percent by weight based on resin solids.

The polyepoxide-polyacid clear film forming compositions according to the present invention are preferably formulated into high solids coating compositions. That is, these film forming compositions contain greater than about 50 percent, most preferably greater than about 60 percent by weight resin solids. The solids content is determined by heating the composition to about 105°-110° C for 1 to 2 hours to drive off the volatile material. The film forming compositions are preferably liquid high solids compositions formulated as either one package or two package compositions. When formulated as a two package composition, the ingredients, including the alkoxy silane polymer, can be in either package as desired so long as the polyepoxide film-former and polyacid curing agent are in separate packages. Preferably the compositions are formulated as one package compositions.

Also, optional ingredients such as auxiliary curing agents such as aminoplast resins, plasticizers, anti-oxidants, and UV light absorbers can be included in the film forming composition. These ingredients typically are present in amounts up to 30 percent by weight based on total resin weight.

When utilizing the clear film forming compositions of the present invention as a topcoat over a pigmented basecoat, in preparing a composite coated substrate, the film-forming composition of the basecoat can be any of the compositions useful in coatings applications, particularly automotive applications, including thermoplastic and thermosetting (crosslinking) coating compositions. The pigmented film-forming composition typically comprises a resinous binder and a pigment. Particularly useful resinous binders are resinous binders known in the art of polymer chemistry such as acrylic polymers, polyester polymers, including alkyds, and polyurethane polymers.

The acrylic polymers are typically copolymers of one or more alkyl esters of acrylic acid or methacrylic acid having from 1 to 20 carbon atoms in the alkyl group optionally together with one or more other polymerizable ethylenically unsaturated monomers. These polymers can be either thermoplastic or thermosetting. Suitable alkyl esters of acrylic acid or methacrylic acid include methyl

methacrylate, isobutyl methacrylate, alpha-methyl styrene dimer, ethyl methacrylate, n-butyl methacrylate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, and 2-ethylhexyl methacrylate. Suitable other copolymerizable ethylenically unsaturated monomers include vinyl aromatic compounds such as styrene and vinyl toluene; nitriles such as acrylonitrile and methacrylonitrile; vinyl and vinylidene halides such as vinyl chloride and vinylidene fluoride and vinyl esters such as vinyl acetate.

When the acrylic polymer is of the crosslinking type, suitable active hydrogen functional monomers are used in addition to the other acrylic monomers mentioned above and include, for example, acrylic acid, methacrylic acid, hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, and hydroxypropyl methacrylate. The coating composition in such cases contains a crosslinking agent capable of reacting with the active hydrogen groups contributed to the polymer by the functional monomers such as aminoplast resins which include condensates of an amine or an amide with such as urea, melamine, or benzoguanamine reacted with formaldehyde or a lower alkyl ether of such condensate in which the alkyl groups contain from 1 to 4 carbon atoms. Other crosslinking agents such as polyisocyanates including blocked polyisocyanates can also be used. Also, the acrylic polymer can be prepared with N-(alkoxymethyl)acrylamide monomer(s) and N-(alkoxymethyl)methacrylamide monomer(s) which result in an acrylic polymer capable of self crosslinking without the presence of crosslinking agents such as those described above.

The acrylic polymer can be prepared by free radical initiated solution polymerization techniques in the presence of suitable free radical initiators such as organic peroxides or azo compounds, for example, benzoyl peroxide or 2,2'-azobis(2-methylbutane nitrile). The polymerization can be carried out in an organic solvent in which the monomers and resultant polymer are soluble. Suitable solvents include aromatic solvents such as xylene and toluene and ketones such as methyl amyl ketone. Alternately, the acrylic polymer can be prepared by aqueous emulsion or dispersion polymerization techniques well known to those skilled in the art.

Besides acrylic polymers, the resinous binder for the basecoat composition can be a polyester polymer (including alkyds). Such polymers may be prepared in a known manner by condensation of polyhydric alcohols and polycarboxylic acids. Suitable polyhydric alcohols include ethylene glycol, propylene glycol, butylene glycol, 1,6-hexylene glycol, neopentyl glycol, diethylene glycol, glycerol, trimethylolpropane, and pentaerythritol.

Suitable polycarboxylic acids include succinic acid, adipic acid, azelaic acid, sebacic acid, maleic acid, fumaric acid, phthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, and trimellitic acid. Besides the polycarboxylic acids mentioned above, functional equivalents of the polycarboxylic acids such as anhydrides where they exist or lower alkyl esters of the polycarboxylic acids such as the methyl esters may be used.

Where it is desired to produce air-drying alkyd resins from the polyester polymer, suitable drying oil fatty acids can be used to modify the polyester by methods well known to those skilled in the art, and include those derived from linseed oil, soya bean oil, tall oil, dehydrated castor oil or tung oil.

The polyester polymers including the alkyd polymers can be thermoplastic or thermosetting. A thermosetting polyester generally contains a portion of free hydroxyl and/or carboxyl groups which are available for crosslinking reaction with a crosslinking agent. Suitable crosslinking agents are the amine or amide-aldehyde condensates or the polyisocyanate curing agents as mentioned above.

Polyurethanes can also be used as the resinous binder of the basecoat. Among the polyurethanes which can be used are polymeric polyols which are prepared by reacting the polyester polyols or acrylic polyols such as those mentioned above with a polyisocyanate such that the OH/NCO equivalent ratio is greater than 1:1 so that free hydroxyl groups are present in the product.

The organic polyisocyanate which is used to prepare the polyurethane polyol can be an aliphatic or an aromatic polyisocyanate or a mixture of the two. Diisocyanates are preferred, although higher polyisocyanates can be used in place of or in combination with diisocyanates.

Examples of suitable aromatic diisocyanates are 4,4'-diphenylmethane diisocyanate and toluene diisocyanate. Examples of suitable aliphatic diisocyanates are straight chain aliphatic diisocyanates such as 1,6-hexamethylene diisocyanate. Also, cycloaliphatic diisocyanates can be employed. Examples include isophorone diisocyanate and 4,4'-methylene-bis(cyclohexyl isocyanate). Examples of suitable higher polyisocyanates are 1,2,4-benzene triisocyanate and polymethylene polyphenyl isocyanate.

The polymers prepared as described above are typically organic solvent-based polymers, although as mentioned above acrylic polymers can be prepared via aqueous emulsion polymerization techniques and used as film forming binders for aqueous-based basecoat compositions. Suitable aqueous-based basecoats for use in color-plus-clear applications are disclosed in U.S. Patent No. 4,403,003, and can be used in the practice of this invention. Also, aqueous-based polyurethanes such as those prepared in accordance with U.S. Patent No. 4,147,679, can be used as the resinous binder of the basecoat.

As mentioned above, the basecoat composition also contains pigments to give it color. Compositions containing metallic flake pigmentation are especially useful for the production of so-called "glamour metallic" finishes chiefly upon the surface of automobile bodies. Proper orientation of the metallic pigments results in a lustrous shiny appearance with excellent flop, distinctness of image and high gloss. By flop is meant the visual change in brightness or lightness of the metallic coating with a change in viewing angle, that is, a change from 90° to 180°. The greater the change, that is, from light to dark appearance, the better the flop. Flop is important because it accentuates the lines of a curved surface such as on an automobile body. Suitable metallic pigments include in particular aluminum flake, copper bronze flake and mica.

Besides the metallic pigments, the basecoat compositions of the present invention can contain non-metallic color pigments conventionally used in coating compositions including inorganic

pigments such as titanium dioxide, iron oxide, chromium oxide, lead chromate and carbon black, and organic pigments such as phthalocyanine blue and phthalocyanine green. In general, the total amount of pigment incorporated into the coating composition is in amounts of from about 1 to about 80 percent by weight based on weight of the resin solids of the composition. The metallic pigment is employed in amounts of about 0.5 to 25 percent by weight of the aforesaid aggregate weight.

If desired, the basecoat composition can additionally contain other materials well known in the art of formulated surface coatings. These would include surfactants, flow control agents, thixotropic agents, fillers, anti-gassing agents, organic co-solvents, catalysts and other customary auxiliaries. These materials can constitute up to 40 percent by weight of the total weight of the coating composition.

The basecoat compositions can be applied to various substrates to which they adhere. The compositions can be applied by conventional means including brushing, dipping, flow coating, spraying and the like, but they are most often applied by spraying. The usual spray techniques and equipment for air spraying and electrostatic spraying and either manual or automatic methods can be used.

Coatings of the present invention can be applied over virtually any substrate including wood, metals, glass, cloth, plastic, foam, including elastomeric substrates, and the like. They are particularly useful in applying over metal and elastomeric substrates that are found on motor vehicles.

During application of the basecoat composition to the substrate, a film of the basecoat is formed on the substrate. Typically, the basecoat thickness will be about 0.05 to 3, preferably 0.1 to 2 mils in thickness.

After application to the substrate of the basecoat composition, a film is formed on the surface of the substrate. This is achieved by driving solvent, i.e., organic solvent or water, out of the basecoat film by heating or simply by an air-drying period. Preferably, the heating step will only be sufficient and for a short

period of time to insure that the topcoat composition can be applied to the basecoat without the former dissolving the basecoat composition, i.e., "striking in". Suitable drying conditions will depend on the particular basecoat composition, on the ambient humidity with certain waterbased compositions, but in general a drying time of from about 1 to 5 minutes at a temperature of about 60°-175°F (15°-79°C) will be adequate to insure that mixing of the two coats is minimized. At the same time, the basecoat film is adequately wetted by the topcoat composition so that satisfactory intercoat adhesion is obtained. Also, more than one basecoat and multiple topcoats may be applied to develop the optimum appearance. Usually between coats, the previously applied basecoat or topcoat is flashed, that is, exposed to ambient conditions for about 1 to about 20 minutes.

After application of a pigmented basecoat as described above, a clear film forming composition of the present invention can be applied to the basecoat by any of the conventional coating techniques such as brushing, spraying, dipping or flow coating, but it is preferred that spray applications be used since such applications give the optimum gloss. Any of the known spray techniques can be employed, such as compressed air spraying, electrostatic spraying and either manual or automatic methods. Prior to application of a topcoat, it is possible to air flash the basecoated substrate for a brief period of time, typically ranging from about 1 to about 5 minutes. Optionally, the coated substrate can be heat flashed between application of a base and topcoat.

After application of the clear topcoat composition to the pigmented basecoat, the coated substrate is heated to cure the coating layers. In the curing operation, solvents are driven off and the film-forming material of the topcoat and/or the basecoat is cured. The heating or curing operation is usually carried out at a temperature in the range of from about 250°F to about 400°F (121°C to 205°C), and more preferably in the range of from about 260°F to about 325°F (127°C to 162°C). Typically, the topcoat is applied at a uniform film thickness usually ranging from about 0.5 to about 5 mils and more preferably from about 1.2 to about 3 mils.

The invention will be further described by reference to the following examples. Unless otherwise indicated, all parts are by weight.

EXAMPLES

The following examples A, B, and C show the preparation of a solution polymer, polyepoxide resin, and polyacid curing agent which are utilized in formulating the clear one package film-forming compositions of examples 1 to 5.

EXAMPLE A

An alkoxy silane solution polymer was prepared from the following mixture of ingredients:

Ingredients	Weight in grams
Initial Charge	
SOLVESSO*-100[1]	1,634.6
Feed 1	
Gamma-methacryloxypropyltrimethoxy silane	4,363.8
n-Butyl methacrylate	1,091.0
Feed 2	
SOLVESSO-100	109.2
Feed 3	
Di-tert-butylperoxide	272.8
SOLVESSO-100	545.6
Feed 4	
SOLVESSO-100	54.6
Feed 5	
Di-tert-butylperoxide	54.4
SOLVESSO-100	109.2
Feed 6	
SOLVESSO-100	54.6

[1] Aromatic hydrocarbon, commercially available from Exxon Chemical Company

The initial charge was heated under nitrogen in a reaction vessel with agitation to reflux temperature (155°C). Feeds 1 and 3 were initiated simultaneously and continued in a substantially continuous manner over a period of 3 hours while maintaining the reaction mixture at reflux temperature. At the completion of Feeds 1 and 3, the addition funnels were rinsed with Feeds 2 and 4, and the reaction mixture was held for 1 hour at reflux temperature. Then Feed 5 was added over 30 minutes and the addition funnel was rinsed with Feed 6. The reaction mixture was held for 2 hours at reflux temperature to complete the polymerization. The reaction mixture was

* Trade-mark

cooled and filtered. The resultant solution polymer had a total solids content of 69.1 percent determined at 110°C for one hour, and a number average molecular weight of 2405 as determined by gel permeation chromatography (GPC) using polystyrene standards. The Gardner-Holdt viscosity was D+.

EXAMPLE B

An epoxy containing acrylic polymer was prepared from the following mixture of ingredients:

Ingredients	Weight in grams
Charge 1	
Xylene	186.1
Ethyl 3-ethoxypropionate[1]	572.9
Charge 2	
Glycidyl methacrylate	1200.0
Methyl methacrylate	11.7
n-Butyl methacrylate	350.1
Styrene	81.7
Alpha-methyl styrene dimer	23.2
Ethyl 3-ethoxypropionate	10.0
Charge 3	
LUPERSOL*555-M60[2]	200.0
Ethyl 3-ethoxypropionate	110.0
Charge 4	
Methyl methacrylate	8.3
n-Butyl methacrylate	250.1
Styrene	58.3
Alpha-methyl styrene dimer	16.6
Ethyl 3-ethoxypropionate	10.0
Charge 5	
t-Butyl perbenzoate	20.0
Ethyl 3-ethoxypropionate	15.0
Charge 6	
t-Butyl perbenzoate	20.0
Ethyl 3-ethoxypropionate	13.7
Charge 7	
t-Butyl perbenzoate	20.0
Ethyl 3-ethoxypropionate	15.0

[1] EKTAPRO* EEP solvent from Eastman Chemicals

[2] t-amyl peracetate (60%) in odorless mineral spirits available from Atochem

Charge 1 was heated in a suitable reactor to reflux. Charge 2 and Charge 3 were added simultaneously to the reaction vessel over a period of about 4 hours then Charge 4 was added over a period of 30 minutes while maintaining the reaction at reflux. At the completion of the additions, the reaction mixture was held at reflux for one

* Trade-mark

hour, cooled to 130°C then Charge 5 was added over a period of 1 hour. The reaction was then held for 30 minutes at reflux. Charge 6 was added over a period of 1 hour and the reaction was held for another 30 minutes at 130° C. Then Charge 7 was added over a period of 1 hour and the reaction was held at 130°C for two hours. The reaction mixture was then cooled to room temperature. The resultant epoxy containing acrylic polymer had a total solids content of about 64.5 percent and a weight average molecular weight of about 2800. The theoretical epoxy equivalent weight based on solids was 237.

EXAMPLE C

A polyacid curing agent was prepared from the following mixture of ingredients:

Ingredients	Weight in grams
Di-Trimethylolpropane	1584.8
Methylhexahydrophthalic anhydride	4120.7
Methyl isobutyl ketone	569.2
n-Propyl alcohol	2117.7

The di-trimethylolpropane and 559.2 grams of methyl isobutyl ketone were charged to a reaction vessel and heated under a nitrogen atmosphere to 115°C. The methylhexahydrophthalic anhydride was added over a period of about 2 hours at 115°C. The remainder of the methyl isobutyl ketone was added as a rinse. The reaction was held at 115°C for 4 hours. The reaction mixture was then cooled to 100°C, and the n-propyl alcohol was added. The reaction mixture was then heated to 105°C and held for 30 minutes and then cooled to room temperature. The resultant product had a solids content of 72.3 percent and an acid value of 163.

EXAMPLE 1

A clear film-forming one package composition was prepared by mixing together the following ingredients:

Ingredients	Weight in grams	Resin Solids
TINUVIN* 328[1]	3.0	3.0
TINUVIN 292[2]	0.4	0.4
Poly (Butyl acrylate)[3]	0.4	0.25
Epoxy containing acrylic from EXAMPLE B	78.0	48.6
Polyacid curing agent from EXAMPLE C	71.0	51.4
Ethyl 3-ethoxypropionate	40.0	

[1] Substituted benzotriazole UV light stabalizer available from Ciba Geigy Co.
[2] Sterically hindered tertiary amine light stabalizer available from Ciba Geigy Co.
[3] Available from E. I. duPont de Nemours and Company

In the following examples 2 to 5, the alkoxy silane polymer of example A was formulated in the clear coating composition of example 1 above, at various levels (5, 10, 15, and 20 percent, respectively based on resin solids). The coating compositions of Examples 1 to 5 were then evaluated for mar resistance over the pigmented basecoat detailed in Example 6 which follows. The details of the evaluation are presented below in Example 6 and the results are tabulated in Table I.

EXAMPLE 2

A clear film forming one package composition was prepared by mixing together the following ingredients:

Ingredients	Weight in grams	Resin Solids
Clear film-forming composition from EXAMPLE 1	192.8	103.65
Alkoxy silane solution polymer from EXAMPLE A	7.3	5.0

* Trade-mark

EXAMPLE 3

A clear film forming one package composition was prepared by mixing together the following ingredients:

Ingredients	Weight in grams	Resin Solids
Clear film-forming composition from EXAMPLE 1	192.8	103.65
Alkoxy silane solution polymer from EXAMPLE A	14.6	10.0

EXAMPLE 4

A clear film forming one package composition was prepared by mixing together the following ingredients:

Ingredients	Weight In grams	Resin Solids
Clear film-forming composition from EXAMPLE 1	192.8	103.65
Alkoxy silane solution polymer from EXAMPLE A	21.9	15.0

EXAMPLE 5

A clear film forming one package composition was prepared by mixing together the following ingredients:

Ingredients	Weight in grams	Resin Solids
Clear film-forming composition from EXAMPLE 1	192.8	103.65
Alkoxy silane solution polymer from EXAMPLE A	29.15	20.0

EXAMPLE 6

A black solventborne acrylic-melamine basecoat, commercially available from PPG Industries, Inc. as NHU-9517, was spray applied to steel test panels (B40, ED 5000 treatments on unpolished steel available from ACT Corporation, Cleveland, Ohio). The basecoat was given a 90 second flash at ambient conditions. Next, two coats of the clear film forming compositions of Examples 1-5 were sprayed applied over the basecoated test panels. The two coats of the various clear film forming compositions were applied wet on wet to the basecoated panels with a two minute flash under ambient conditions between coats. After a final 5 minute flash at ambient conditions the test panels were baked at 285°F (141°C) for 30 minutes. The total film thickness of the basecoat was about 0.8 mil., and the total film thickness of the various clearcoats was between about 1.5 to 1.8 mil. The panels were then tested for mar resistance using the following procedure.

1. Dry Bon-Ami* Cleanser (Feldspar/Calcite cleanser manufactured by Faultless Starch/Bon Ami Company, Kansas City, MO) was applied to one half of the test panel.
2. The excess cleanser was tapped off so that a thin film of cleanser remained on the test panel.
3. The acrylic finger of an Atlas AATCC Crockmeter, model CM-5 manufactured by Atlas Electric Devices Company, Chicago, Illinois, was covered with a two inch by two inch piece of felt cloth, obtainable from Atlas Electric Devices.
4. The cleanser coated panel was rubbed with the felt cloth ten times (ten double rubs) using the Crockmeter.
5. The test was repeated at least once changing the felt cloth after each test.
6. After testing, the panel was washed with water to remove the cleanser and then carefully dried.

* Trade-mark

7. The 20° gloss was measured using a gloss meter manufactured by Byk-Gardner Inc., Silver Spring MD, on both the unmarred part of the panel and the marred parts of the panel. The difference in gloss was a measure of the mar resistance. The smaller the difference the greater the mar resistance.

The test results are listed in the following table:

TABLE I

Example	Basecoat Thickness in mils	Clearcoat Thickness in mils	DOI[1]	20° Gloss		
				Unmarred Panel Section	Marred Panel Section	Difference
1	0.8	1.8	94	82	47	35
2	0.8	1.7	90	82	57	25
3	0.8	1.7	86	82	63	19
4	0.8	1.5	84	82	63	19
5	0.8	1.7	93	82	60	22

[1] Determined by Dori-Gon Meter D47-6 manufactured by Hunter Laboratories

Examples 3 and 4 exhibited the best improvement in mar resistance in that they lost only 19 units of gloss when subjected to the mar test described above. These results can be compared to Example 1, which contains no alkoxy silane polymer additive, and a difference of 35 units in gloss when subjected to the mar test.

The following examples D, E, F, G, H, and I show preparation of a solution polymer, polyepoxide resin, polyacid curing agents, and fumed silica resin dispersion which are used in the preparation of a two package film forming composition of Example 7.

EXAMPLE D

An alkoxy silane solution polymer was prepared from the following mixture of ingredients:

Ingredients	Weight in grams
Charge 1	
SOLVESSO-100	101.2
Charge 2	
Di-tert-butylperoxide	40.6
SOLVESSO-100	20.3
Charge 3	
Gamma-Methacryloxypropyltrimethoxy silane	270.1
n-Butyl methacrylate	57.4
Styrene	3.4
Methyl methacrylate	3.4
2-Ethylhexyl acrylate	3.4
Charge 4	
SOLVESSO-100	6.8
Charge 5	
SOLVESSO-100	6.8

Charge 1 was heated under nitrogen in a reaction vessel with agitation to reflux temperature (155°C). At reflux the addition of 50.7 grams from Charge 2 was started to the reaction vessel over 3 hours. Five minutes after beginning the addition of Charge 2, the addition of Charge 3 was initiated and continued in a substantially continuous manner over a period of 3 hours while maintaining the reaction mixture at reflux temperature. At the completion of the addition of Charge 3 the tank and lines were rinsed with Charge 4, and the reaction mixture was held for 1 hour at reflux temperature. The remaining 10.2 grams of Charge 2 was then added to the reactor over a period of 30 minutes and then the tank and lines were rinsed with Charge 5, and the reaction mixture was held for 2 hours at reflux temperature to complete the polymerization. The reaction mixture was cooled and filtered. The resultant polymer had a total solids content of 69.6 percent determined at 110°C for one hour and number average molecular weight of 1703 as determined by gel permeation chromatography (GPC) using polystyrene standards.

EXAMPLE E

An epoxy containing acrylic resin was prepared from the following mixture of ingredients:

Ingredients	Weight in Grams
Charge 1	
Xylene	3196.0
Charge 2	
Glycidyl methacrylate	2160.0
Methyl methacrylate	1782.0
n-Butyl Acrylate	1350.0
Styrene	108.0
Xylene	30.0
Charge 3	
VAZO*-67[1]	162.0
t-Butyl perbenzoate	108.0
Xylene	330.0
Charge 4	
t-Butyl perbenzoate	27.0
Xylene	130.0
Charge 5	
t-Butyl perbenzoate	27.0
Xylene	130.0

[1] 2, 2' azobis(2-methylbutane) nitrile available from E. I. duPont de Nemours and Company

Charge 1 was placed into a suitable reactor and heated under a nitrogen atmosphere to reflux. Charge 2 and charge 3 were added simultaneously to the reaction vessel over a period of 3 hours and then the reaction was held at reflux for 30 minutes. Charge 4 was then added over 30 minutes and the reaction mixture was held at reflux for 30 minutes. Finally charge 5 was added over 30 minutes and the reaction mixture was then held at reflux for 2 hours. The reaction mixture was then cooled to room temperature. The reaction mixture had a total solids content of about 59.5 and a weight average molecular weight of about 5831.

* Trade-mark

EXAMPLE F

A polyacid resin was prepared from the following mixture of ingredients:

Ingredients	Weight in grams
Charge 1	
Trimethylolpropane	134.1
Hexahydrophthalic anhydride	151.1
Methyl isobutyl ketone	244.0
Charge 2	
Methylhexahydrophthalic anhydride	352.5
Methyl isobutyl ketone	20.0
Charge 3	
Ethyl alcohol	9.3

Charge 1 was placed into a suitable reactor and heated under a nitrogen atmosphere to 115°C. Charge 2 was added over 1 to 2 hours, the reaction mixture was held at 115°C for 4 hours, and then cooled to 100°C followed by the addition of Charge 3. The reaction mixture was then heated to 105°C, held for 30 minutes, and then cooled to room temperature. The reaction mixture had a solids content of 69.5 percent and an acid value of 189.5.

EXAMPLE G

A polyacid resin was prepared from the following mixture of ingredients:

Ingredients	Weight in grams
Charge 1	
Ester Diol 204[1]	2856.0
Hexahydrophthalic anhydride	1336.7
Methyl isobutyl ketone	1725.1
Charge 2	
Methylhexahydrophthalic anhydride	3155.2
Methyl isobutyl ketone	20.0
Charge 3	
ethyl alcohol	91.9

[1] 1-(3-hydroxy-2,2-dimethylpropyl)-3-hydroxy-2,2-dimethylpropionate available from Shell

Charge 1 was placed in a suitable reactor and heated under a nitrogen atmosphere to 115°C. Charge 2 was added over 1 to 2 hours and then the reaction mixture was held at 115°C for 4 hours, and then cooled to 100°C followed by the addition of Charge 3. The reaction mixture was then heated to 105°C, held for 30 minutes, and then cooled to room temperature. The reaction mixture had a solids content of 79.5 percent and an acid value of 167.6.

EXAMPLE H

An anhydride copolymer was prepared from the following mixture of ingredients:

Ingredients	Weight in grams
Charge 1	
1-Octene	1246.0
Charge 2	
LUPERSOL 555-M60	363.4
Butyl acetate	18.5

Charge 3

Maleic anhydride	545.1
Butyl acetate	1308.3
Butyl acetate	18.5

Charge 1 was placed in a suitable reactor and heated under a nitrogen atmosphere to reflux. Charge 2 and charge 3 were added simultaneously over a period of 2 hours and the reaction mixture was then held at reflux for 1 hour, and then heated to 130°C and held for 1 hour. The reaction mixture was then cooled to room temperature. The reaction mixture had a total solids content of 73.3 percent.

EXAMPLE I

A fumed silica grind was prepared by mixing the following ingredients, grind loading the mixture into a mill and grinding to a number 7 Hegman.

Ingredients	Weight in grams
RESIMENE* HM-7554[1]	360.1
n-amyl alcohol	395.7
AEROSIL* R812[2]	65.7

[1] Aminoplast resin available from Monsanto
[2] Hydrophobic silicon dioxide available from Degussa

EXAMPLE 7

A clear film-forming two package composition was prepared by mixing together the following ingredients:

Ingredients	Weight in grams	Resin Solids
Pack - A		
DOWANOL* DPM[1]	5.0	
TINUVIN 328	2.65	2.65
TINUVIN 292	0.35	0.35
Poly(Butyl acrylate)	0.42	0.25
MULTIFLOW[2]*	0.50	0.25
ERL-4221[3]	19.0	19.0
RESIMENE 717[4]	13.3	10.6

* Trade-mark

Acrylic resin from EXAMPLE E	32.4	29.0
Fumed silica grind from EXAMPLE I	8.1	2.9
Pack - B		
Polyacid polymer from EXAMPLE F	34.3	24.0
Polyacid polymer from EXAMPLE H	15.1	11.0
Polyacid polymer from EXAMPLE G	11.9	9.5
Isostearic acid	4.0	4.0
DM-12D[5]	4.0	4.0
Methyl isobutyl ketone	8.0	
Hexyl acetate[6]	8.0	

[1] Dipropylene glycol monomethyl ether available from Dow Chemical
[2] 50% solution of ethyl acrylate/2-ethyl hexyl acrylate copolymer available from Monsanto
[3] Dicycloaliphatic epoxide available from Union Carbide
[4] Aminoplast resin available from Monsanto
[5] N,N-Dimethyl-1-Aminododecane avilable from Akzo Chemical
[6] EXXATE* 600 available from Exxon Company

* Trade-mark

In the following examples 8 and 9, the alkoxy silane polymer of example A was formulated in the clear film forming composition of example 7 above, at various levels (5 and 10 percent, respectively based on resin solids). These coating compositions were then evaluated for mar resistance over the pigmented basecoat detailed in Example 10 which follows. The details of the evaluation are presented below in Example 10 and the results tabulated in Table II.

EXAMPLE 8

A clear film forming two package composition was prepared by mixing together the following ingredients:

Ingredients	Weight in grams	Resin Solids
Clear film forming composition from EXAMPLE 7	167.0	104.0
Alkoxy silane solution polymer from EXAMPLE D	7.1	5.0

EXAMPLE 9

A clear film forming two package composition was prepared by mixing together the following ingredients:

Ingredients	Weight in grams	Resin Solids
Clear film forming composition from EXAMPLE 7	167.0	104.0
Alkoxy silane solution polymer from EXAMPLE D	14.2	10.0

EXAMPLE 10

A black solventborne acrylic-melamine basecoat, commercially available from PPG Industries, Inc. as NHU-9517, was spray applied to steel test panels (B40, ED 5000 treatments on unpolished steel available from ACT Corporation, Cleveland, Ohio). The basecoat was given a 90 second flash at ambient conditions. Next two coats of the clear film forming compositions of Examples 7-9 were sprayed applied over the basecoated test panels. The two coats of the various clear film forming compositions were applied wet on wet to the basecoated panels with a two minute flash under ambient conditions between coats. After a final 5 minute flash at ambient conditions the test panels were baked at 250°F (121°C) for 30 minutes. The total film thickness of the basecoat was about 0.8 mil., and the total film thickness of the various clearcoats was between about 1.5 to 1.8 mil. The panels were then tested for mar resistance using the procedure described in Example 6 above.

The test results are listed in the following table.

TABLE II

				20° Gloss		
Example	Basecoat Thickness in mils	Clearcoat Thickness in mils	DOI[1]	Unmarred Panel Section	Marred Panel Section	Difference
7	0.8	1.8	97.8	84	59	25
8	0.8	1.7	97.3	84	68	16
9	0.8	1.7	94.1	84	69	15

[1] Determined by Dori-Gon Meter D47-6 manufactured by Hunter Laboratories

Examples 8 and 9 exhibited improved mar resistance in that they lost only 16 and 15 units of gloss, respectively when subjected to the mar test described above. These results can be compared to Example 7, which contains no alkoxy silane polymer additive, and a difference of 25 units in gloss when subjected to the mar test.

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CLAIMS:

1. A film forming composition, comprising:

10 to 90 percent by weight, based on the total weight of resin solids, of a polyepoxide polymer which contains no more than 1% silicon, based on the weight of the polyepoxide polymer;

10 to 90 percent by weight, based on total weight of resin solids, of a polyacid curing agent; and

1 to 20 percent by weight, based on total weight of resin solids, of a solution polymer made from polymerizable ethylenically unsaturated monomers, the monomers comprising 60 to 100 percent by weight, based on total weight of the monomers, of a polymerizable ethylenically unsaturated alkoxy silane monomer.

2. The composition of claim 1 wherein the ethylenically unsaturated monomers from which the solution polymer is made additionally comprise at least one other polymerizable ethylenically unsaturated monomer.

3. The composition of claim 2 wherein the polymerizable alkoxy silane monomer is selected from gamma-methacryloxypropyltrimethoxysilane, gamma-methacryloxypropyltriethoxysilane, gamma-methacryloxypropyltris(2-methoxyethoxy) silane, and mixtures thereof.

4. The composition of claim 3 wherein the other ethylenically unsaturated monomer is selected from the group consisting of alkyl acrylates, alkyl methacrylates, vinyl aromatic monomers, and acrylonitrile.

5. The composition of claim 4 wherein the other ethylenically unsaturated monomer is an alkyl methacrylate selected from the group consisting of methyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, styrene and 2-ethylhexyl methacrylate.

6. The composition of claim 5 wherein the solution polymer is a copolymer of gamma-methacryloxypropyltrimethoxysilane and n-butyl methacrylate.

7. The composition of claim 1 wherein the solution polymer is present in the film forming composition in an amount from about 10 to about 20 percent by weight, the percentage based on total weight of resin solids of the film forming composition.

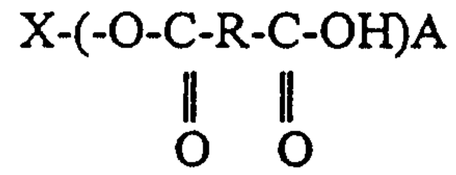
8. The composition of claim 1 wherein the solution polymer has a number average molecular weight of between about 500 and about 20,000.

9. The composition of claim 1, wherein the polyepoxide is a copolymer of at least one monoethylenically unsaturated monomer having at least one epoxy group and at least one monoethylenically unsaturated monomer which is free of epoxy groups.

10. The composition of claim 9, in which the polyepoxide copolymer is a copolymer of glycidyl acrylate or glycidyl methacrylate with at least one other copolymerizable ethylenically unsaturated monomer.

11. The composition of claim 10, in which the other copolymerizable ethylenically unsaturated monomer comprises at least in part an alkyl ester of acrylic or methacrylic acid containing from 1 to 20 carbon atoms in the alkyl group.

12. The composition of claim 1, wherein the polyacid curing agent is a half-ester of the structure:



where X is a residue of a polyol after the polyol has been reacted with a 1,2-dicarboxylic acid anhydride, R is an organic moiety from the anhydride, and A is an integer of at least two.

13. The composition of claim 12, wherein said polyol is selected from the group consisting of di-trimethylol propane, pentaerythritol, 1,2,3,4-butanetetrol, sorbitol, trimethylol propane, trimethylol ethane, 1,6-hexanediol, 1,2,6-hexanetriol, 1,3,6-hexanetriol, glycerin, trishydroxyethyl isocyanurate, dimethylol propionic acid, 1,2,4-butanetriol, 1,3,4-butanetriol, neopentyl glycol, and mixtures thereof.

14. The composition of claim 12 in which the 1,2-dicarboxylic acid anhydride is selected from the group consisting of hexahydrophthalic anhydride and alkyl-substituted hexahydophthalic anhydrides.

15. The composition of claim 1 wherein the equivalent ratio of acid in the polyacid curing agent to epoxy in the polyepoxide ranges from about 0.3:1 to about 3:1.

16. The composition of claim 1, wherein said composition has a resin solids content of at least about 40 percent.

17. The composition of claim 1 further comprising an amount up to 50 percent by weight of the composition, the percentages based on the total weight of resin solids of the composition, of a carboxylic acid functional acrylic polymer having a number average molecular weight of from about 500 to about 5000.

18. The composition of claim 1 further comprising an aminoplast resin.

19. The composition of claim 18 wherein the aminoplast resin is present in the composition in an amount up to 30 percent by weight of the composition, the percentage based on total weight resin solids of the coating composition.

20. The composition of claim 1 in which the film forming composition is a clear film forming composition.

21. A method for applying a composite coating to a substrate which comprises:

(I) applying to the surface of the substrate a pigmented film-forming composition;

(II) allowing the composition applied in step (I) to at least partially dry or cure to form a base coat on the surface;

(III) applying to said base coat a clear film-forming composition of claim 1;

(IV) allowing the clear composition to at least partially dry or cure to form a transparent topcoat over said basecoat.