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(71) **Applicant: PPG INDUSTRIES OHIO, INC.** [US/US]; 3800 West 143rd Street, Cleveland, Ohio 44111 (US).

(72) **Inventors: MORAVEK, Scott J.**; 153 Briarwood Lane, Cranberry Township, Pennsylvania 16066 (US). **MOHNOT, Shantilal**; 1016 Summer Ridge Court, Murrysville, Pennsylvania 15668 (US). **THOMAS, Stephen J.**; 309 Center Avenue, Aspinwall, Pennsylvania 15215 (US).

(74) **Agents: TREBILCOCK, Christine W.** et al.; PPG Industries, Inc., One PPG Place, 39th Floor, Pittsburgh, Pennsylvania 15272 (US).

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(54) **Title:** CURABLE FILM-FORMING COMPOSITIONS DEMONSTRATING BURNISH RESISTANCE AND LOW GLOSS

(57) **Abstract:** The present invention is directed to curable film-forming compositions comprising: (a) a polymeric binder comprising at least one polymeric resin having reactive functional groups; (b) a curing agent containing functional groups that are reactive with the reactive functional groups of (a); an d (c) silica particles that have been functionalized on their surfaces with an amino silane so as to impart the surfaces with primary amino functional groups. After application to a substrate as a coating and after curing, the curable film-forming composition demonstrates an initial 85 gloss of less than 30 and an increase in 85 gloss of no more than 15 gloss units when subjected to various ABRASION TEST METHODS as defined herein.

CURABLE FILM-FORMING COMPOSITIONS DEMONSTRATING BURNISH RESISTANCE AND LOW GLOSS

FIELD OF THE INVENTION

[0001] The present invention relates generally to curable film-forming compositions that demonstrate burnish resistance and low gloss properties.

BACKGROUND OF THE INVENTION

[0002] Recently a great deal of research effort in the coatings industry has been focused on mar and abrasion resistance of transparent coatings. While these two terms are often used interchangeably, the physical and mechanistic events are quite different. Mar is a near-surface phenomenon involving small scratches, usually without significant removal of material. Abrasion involves much more severe damage and often entails significant loss of coating material. As such, mar resistance is influenced primarily by surface properties while abrasion resistance is controlled by bulk properties. The chemical attributes that influence these mechanical properties are often divergent. For example, acrylic urethane clearcoats can have excellent abrasion resistance but poor mar resistance. On the other hand, acrylic melamine coatings can have good mar resistance and average to poor abrasion resistance. One common example of mar damage is gloss loss on an automobile finish. The high gloss finish of a new car becomes dull and hazy with time due to fine scratches and abrasions. The majority of this damage is caused by the scrubbing action of cloths or bristles used in automatic car washes. Abrasion damage is more commonly seen in floor coatings, and in its most severe form the substrate may become exposed. Burnishing of highly pigmented coatings is less well defined in the literature but contains elements of mar and abrasion as well as interfacial adhesion. There are at least four different wearing mechanisms that can contribute to burnishing in coatings containing fillers or pigments. 1) Removal of film at the air/surface interface, 2) abstraction of the filler by cohesive binder failure, 3) abstraction of filler by adhesive failure and/or 4) filler wear. Which mechanism predominates may vary depending on the coating, abrasion conditions and outdoor exposure. Ideally a burnish resistant coating has good abrasion resistance, good mar resistance, and pigment particles with excellent compatibility with the binder.

[0003] Camouflage aircraft typically utilize low gloss pigmented coatings to achieve many of their performance requirements. These low gloss or matte finishes exhibit physically rough surfaces, which, ideally, diffusely reflect visible light. These physically rough surfaces are difficult to clean and often require scrubbing with an abrasive pad, which over time can increase the uniformity of coating reflectance, called burnishing. The increase in reflection is perceived visually as a color shift resulting in areas of higher contrast. Mechanically, this increase in gloss or burnishing is caused by abrasion of the rough paint surface producing a smoother surface with more uniform reflection.

[0004] It would be desirable to develop curable film-forming compositions which can be repeatedly cleaned with detergents and abrasives without increasing the reflectance of the coating.

SUMMARY OF THE INVENTION

[0005] The present invention is directed to curable film-forming compositions comprising:

(a) a polymeric binder comprising at least one polymeric resin having reactive functional groups;

(b) a curing agent containing functional groups that are reactive with the reactive functional groups of (a); and

(c) silica particles that have been functionalized on their surfaces with an amino silane so as to impart the surfaces with primary amino functional groups. After application to a substrate as a coating and after curing, the curable film-forming composition demonstrates an initial 85° gloss of less than 30 and an increase in 85° gloss of no more than 10 gloss units when subjected to various ABRASION TEST METHODS as defined herein.

DETAILED DESCRIPTION OF THE INVENTION

[0006] It is noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless expressly and unequivocally limited to one referent.

[0007] Other than in the operating examples, or where otherwise indicated, all numbers or expressions referring to quantities of ingredients, reaction conditions, etc., used in the specification and claims are to be understood as modified in all instances by the term “about”. Various numerical ranges are disclosed in this patent application. Because these ranges are continuous, they include every value between the minimum and maximum values. Unless expressly indicated otherwise, the various numerical ranges specified in this application are approximations.

[0008] The various embodiments and examples of the present invention as presented herein are each understood to be non-limiting with respect to the scope of the invention.

[0009] As used in the following description and claims, the following terms have the meanings indicated below:

[0010] The terms “acrylic” and “acrylate” are used interchangeably (unless to do so would alter the intended meaning) and include acrylic acids, anhydrides, and derivatives thereof, such as their C1-C5 alkyl esters, lower alkyl-substituted acrylic acids, e.g., C1-C5 substituted acrylic acids, such as methacrylic acid, ethacrylic acid, etc., and their C1-C5 alkyl esters, unless clearly indicated otherwise. The terms “(meth)acrylic” or “(meth)acrylate” are intended to cover both the acrylic/acrylate and methacrylic/methacrylate forms of the indicated material, e.g., a (meth)acrylate monomer.

[0011] The term "curable", as used for example in connection with a curable composition, means that the indicated composition is polymerizable or cross linkable through functional groups, e.g., by means that include, but are not limited to, thermal (including ambient cure) and/or catalytic exposure.

[0012] The term “cure”, “cured” or similar terms, as used in connection with a cured or curable composition, e.g., a “cured composition” of some specific description, means that at least a portion of the polymerizable and/or crosslinkable components that form the curable composition is polymerized and/or crosslinked. Additionally, curing of a polymerizable composition refers to subjecting said composition to curing conditions such as but not limited to thermal curing, leading to the reaction of the reactive functional groups of the composition, and resulting in polymerization and formation of a polymerizate. When a polymerizable composition is subjected to curing conditions, following polymerization and after reaction of most of the reactive end groups occurs, the rate of reaction of the remaining unreacted reactive end groups becomes progressively slower. The polymerizable composition can be subjected to curing conditions until it is at least partially cured. The term “at least partially cured” means subjecting the polymerizable composition to curing conditions, wherein reaction of at least a portion of the reactive groups of the composition occurs, to form a polymerizate. The polymerizable composition can also be subjected to curing conditions such that a substantially complete cure is attained and wherein further curing results in no significant further improvement in polymer properties, such as hardness.

[0013] The term “reactive” refers to a functional group capable of undergoing a chemical reaction with itself and/or other functional groups spontaneously or upon the application of heat or in the presence of a catalyst or by any other means known to those skilled in the art.

[0014] The term “burnish resistant” refers to an ability of a coating to maintain its gloss without demonstrating a significant increase (i. e., less than 15 points) in gloss after scrubbing with an abrasive material or pad.

[0015] The present invention is directed to curable film-forming compositions. The film-forming compositions comprise (a) a polymeric binder comprising at least one polymeric resin having reactive functional groups. Examples of reactive functional groups include hydroxyl groups, carbamate groups, carboxyl groups, isocyanate groups, carboxylate groups, primary amine groups, secondary amine groups, amide groups, urea groups, urethane groups, epoxy groups, and combinations thereof.

[0016] Particularly useful polymeric film-forming resins suitable as the polymeric binder (a) are acrylic polymers, polyesters, including alkyds, and polyurethanes. Generally these polymers can be any polymers of these types made by any method known to those skilled in the art where the polymers are water dispersible or emulsifiable and preferably of limited water solubility.

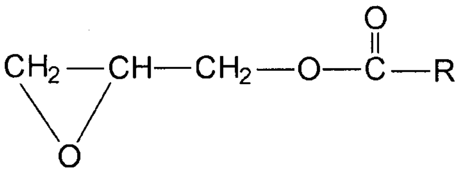
[0017] Suitable acrylic polymers include copolymers of one or more alkyl esters of acrylic acid or methacrylic acid, optionally together with one or more other polymerizable ethylenically unsaturated monomers. Useful alkyl esters of acrylic acid or methacrylic acid include aliphatic alkyl esters containing from 1 to 30, and preferably 4 to 18 carbon atoms in the alkyl group. Non-limiting examples include methyl methacrylate, ethyl methacrylate, butyl methacrylate, ethyl acrylate, butyl acrylate, and 2-ethyl hexyl acrylate. 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.

[0018] The acrylic copolymer can include hydroxyl functional groups, which are often incorporated into the polymer by including one or more hydroxyl functional monomers in the reactants used to produce the copolymer. Useful hydroxyl functional monomers include hydroxyalkyl acrylates and methacrylates, typically having 2 to 4 carbon atoms in the hydroxyalkyl group, such as hydroxyethyl acrylate, hydroxypropyl acrylate, 4-hydroxybutyl acrylate, hydroxy functional adducts of caprolactone and hydroxyalkyl acrylates, and corresponding methacrylates, as well as the beta-hydroxy ester functional monomers described below. The acrylic polymer can also be prepared with N-(alkoxymethyl)acrylamides and N-(alkoxymethyl)methacrylamides.

[0019] Beta-hydroxy ester functional monomers can be prepared from ethylenically unsaturated, epoxy functional monomers and carboxylic acids having from about 13 to about 20 carbon atoms, or from ethylenically unsaturated acid functional monomers and epoxy compounds containing at least 5 carbon atoms which are not polymerizable with the ethylenically unsaturated acid functional monomer.

[0020] Useful ethylenically unsaturated, epoxy functional monomers used to prepare the beta-hydroxy ester functional monomers include, but are not limited to, glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether, methallyl glycidyl ether, 1:1 (molar) adducts of ethylenically unsaturated monoisocyanates with hydroxy functional monoepoxides such as glycidol, and glycidyl esters of polymerizable polycarboxylic acids such as maleic acid. Glycidyl acrylate and glycidyl methacrylate are preferred. Examples of carboxylic acids include, but are not limited to, saturated monocarboxylic acids such as isostearic acid and aromatic unsaturated carboxylic acids.

[0021] Useful ethylenically unsaturated acid functional monomers used to prepare the beta-hydroxy ester functional monomers include monocarboxylic acids such as acrylic acid, methacrylic acid, crotonic acid; dicarboxylic acids such as itaconic acid, maleic acid and fumaric acid; and monoesters of dicarboxylic acids such as monobutyl maleate and monobutyl itaconate. The ethylenically unsaturated acid functional monomer and epoxy compound are typically reacted in a 1:1 equivalent ratio. The epoxy compound does not contain ethylenic unsaturation that would participate in free radical-initiated polymerization with the unsaturated acid functional monomer. Useful epoxy compounds include 1,2-pentene oxide, styrene oxide and glycidyl esters or ethers, preferably containing from 8 to 30 carbon atoms, such as butyl glycidyl ether, octyl glycidyl ether, phenyl glycidyl ether and para-(tertiary butyl) phenyl glycidyl ether. Preferred glycidyl esters include those of the structure:



[0022] where R is a hydrocarbon radical containing from about 4 to about 26 carbon atoms. Preferably, R is a branched hydrocarbon group having from about 8 to about 10 carbon atoms, such as neopentanoate, neoheptanoate or neodecanoate. Suitable glycidyl esters of carboxylic acids include VERSATIC ACID 911 and CARDURA E, each of which are commercially available from Shell Chemical Co.

[0023] Carbamate functional groups can be included in the acrylic polymer by copolymerizing the acrylic monomers with a carbamate functional vinyl monomer, such as a carbamate functional alkyl ester of methacrylic acid, or by reacting a hydroxyl functional acrylic polymer with a low molecular weight carbamate functional material, such as can be derived from an alcohol or glycol ether, via a transcarbamoylation reaction. Alternatively, carbamate functionality may be introduced into the acrylic polymer by reacting a hydroxyl functional acrylic polymer with a low molecular weight carbamate functional material, such as can be derived from an alcohol or glycol ether, via a transcarbamoylation reaction. In this reaction, a low molecular weight carbamate functional material derived from an alcohol or glycol ether is reacted with the hydroxyl groups of the acrylic polyol, yielding a carbamate functional acrylic polymer and the original alcohol or glycol ether. The low molecular weight carbamate functional material derived from an alcohol or glycol ether may be prepared by reacting the alcohol or glycol ether with urea in the presence of a catalyst. Suitable alcohols include lower molecular weight aliphatic, cycloaliphatic, and aromatic alcohols such as methanol, ethanol, propanol, butanol, cyclohexanol, 2-ethylhexanol, and 3-methylbutanol. Suitable glycol ethers include ethylene glycol methyl ether and propylene glycol methyl ether. Propylene glycol methyl ether and methanol are most often used. Other useful carbamate functional monomers are disclosed in U.S. Patent No. 5,098,947, which is incorporated herein by reference. Other useful carbamate functional monomers are disclosed in U.S. Patent No. 5,098,947, which is incorporated herein by reference.

[0024] Amide functionality may be introduced to the acrylic polymer by using suitably functional monomers in the preparation of the polymer, or by converting other functional groups to amido- groups using techniques known to those skilled in the art. Likewise, other functional groups may be incorporated as desired using suitably functional monomers if available or conversion reactions as necessary.

[0025] Acrylic polymers can be prepared via aqueous emulsion polymerization techniques and used directly in the preparation of the aqueous coating compositions, or can be prepared via organic solution polymerization techniques with groups capable of salt formation such as acid or amine groups. Upon neutralization of these groups with a base or acid the polymers can be dispersed into aqueous medium. Generally any method of producing such polymers that is known to those skilled in the art utilizing art recognized amounts of monomers can be used.

[0026] In particular embodiments of the present invention, the polymeric binder (a) comprises a mixture of two hydroxyl functional acrylic polymers. The first comprises a polymerization product of styrene, hydroxypropyl acrylate, isostearic acid, glycidyl methacrylate, and methyl methacrylate as referenced in US 5,869,566, Examples 1-16, which is incorporated herein by reference while the second comprises a polymerization product of hydroxypropyl methacrylate, methyl methacrylate, n-butyl acrylate, styrene, Cardura E/acrylic acid adduct, and acrylic acid according to US 6,458,885, which is incorporated herein by reference and the two are mixed in a weight ratio in the range of 1:1 to 3:1, respectively.

[0027] Besides acrylic polymers, the polymeric film-forming resin suitable as the polymeric binder (a) in the coating composition may be an alkyd resin or a polyester. Such polymers may be prepared in a known manner by condensation of polyhydric alcohols and polycarboxylic acids. Suitable polyhydric alcohols include, but are not limited to, ethylene glycol, propylene glycol, butylene glycol, 1,6-hexylene glycol, neopentyl glycol, diethylene glycol, glycerol, trimethylol propane, and pentaerythritol. Suitable polycarboxylic acids include, but are not limited to, 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 acids such as anhydrides where they exist or lower alkyl esters of the acids such as the methyl esters may be used.

[0028] Useful alkyd resins include polyesters of polyhydroxyl alcohols and polycarboxylic acids chemically combined with various drying, semi-drying and non-drying oils in different proportions. Thus, for example, the alkyd resins are made from polycarboxylic acids such as phthalic acid, maleic acid, fumaric acid, isophthalic acid, succinic acid, adipic acid, azeleic acid, sebacic acid as well as from anhydrides of such acids, where they exist. The polyhydric alcohols which can be reacted with the polycarboxylic acid include 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, ethylene glycol, diethylene glycol and 2,3-butylene glycol, glycerol, trimethylolpropane, pentaerythritol, sorbitol and mannitol.

[0029] The alkyd resins are produced by reacting the polycarboxylic acid and the polyhydric alcohol together with a drying, semi-drying or non-drying oil in proportions depending upon the properties desired. The oils are coupled into the resin molecule by esterification during manufacturing and become an integral part of the polymer. The oil is fully saturated or predominately unsaturated. When cast into films, fully saturated oils tend to give a plasticizing effect to the film, whereas predominately unsaturated oils tend to crosslink and dry rapidly with oxidation to give more tough and solvent resistant films. Suitable oils include coconut oil, fish oil, linseed oil, tung oil, castor oil, cottonseed oil, safflower oil, soybean oil, and tall oil. Various proportions of the polycarboxylic acid, polyhydric alcohol and oil are used to obtain alkyd resins of various properties as is well known in the art.

[0030] Carbamate functional groups may be incorporated into the polyester by first forming a hydroxyalkyl carbamate which can be reacted with the polyacids and polyols used in forming the polyester. The hydroxyalkyl carbamate is condensed with acid functionality on the polyester, yielding terminal carbamate functionality. Carbamate functional groups may also be incorporated into the polyester by reacting terminal hydroxyl groups on the polyester with a low molecular weight carbamate functional material via a transcarbamoylation process similar to the one described above in connection with the incorporation of carbamate groups into the acrylic polymers, or by reacting isocyanic acid with a hydroxyl functional polyester.

[0031] Other functional groups such as amide, thiol, urea, and thiocarbamate may be incorporated into the polyester or alkyd resin as desired using suitably functional reactants if available, or conversion reactions as necessary to yield the desired functional groups. Such techniques are known to those skilled in the art.

[0032] Polyurethanes can also be used as the polymeric binder (a) in the film-forming composition of the present invention. Among the polyurethanes which can be used are polymeric polyols which generally 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. As with the polyesters, the polyurethanes can be prepared with unreacted carboxylic acid groups, which upon neutralization with bases such as amines allows for dispersion into aqueous medium.

[0033] Terminal and/or pendent carbamate functional groups can be incorporated into the polyurethane by reacting a polyisocyanate with a polymeric polyol containing the terminal/pendent carbamate groups. Alternatively, carbamate functional groups can be incorporated into the polyurethane by reacting a polyisocyanate with a polyol and a hydroxyalkyl carbamate or isocyanic acid as separate reactants. Carbamate functional groups can also be incorporated into the polyurethane by reacting a hydroxyl functional polyurethane with a low molecular weight carbamate functional material via a transcarbamoylation process similar to the one described above in connection with the incorporation of carbamate groups into the acrylic polymer. Additionally, an isocyanate functional polyurethane can be reacted with a hydroxyalkyl carbamate to yield a carbamate functional polyurethane.

[0034] Other functional groups such as amide, thiol, urea, and thiocarbamate may be incorporated into the polyurethane as desired using suitably functional reactants if available, or conversion reactions as necessary to yield the desired functional groups. Such techniques are known to those skilled in the art.

[0035] The amount of the polymer present in the polymeric binder (a) generally ranges from 10 to 90 percent by weight, such as 20 to 80 percent by weight, or 40 to 60 percent by weight, based on the total weight of resin solids (curing agent plus all polymers containing functional groups) in the film-forming composition.

[0036] The curable film-forming compositions of the present invention further comprise a curing agent (b) comprising functional groups that are reactive with the reactive functional groups of (a). The curing agent (b) may be selected from, for example, polyisocyanates and aminoplasts. Mixtures of curing agents may also be used.

[0037] Useful aminoplast resins are based on the addition products of formaldehyde with an amino- or amido-group carrying substance. Condensation products obtained from the reaction of alcohols and formaldehyde with melamine, urea or benzoguanamine are most common and preferred herein. While the aldehyde employed is most often formaldehyde, other similar condensation products can be made from other aldehydes, such as acetaldehyde, crotonaldehyde, acrolein, benzaldehyde, furfural, glyoxal and the like.

[0038] Condensation products of other amines and amides can also be used, for example, aldehyde condensates of triazines, diazines, triazoles, guanadines, guanamines and alkyl- and aryl-substituted derivatives of such compounds, including alkyl- and aryl-substituted ureas and alkyl- and aryl-substituted melamines. Non-limiting examples of such compounds include N,N'-dimethyl urea, benzourea, dicyandiamide, formaguanamine, acetoguanamine, glycoluril, ammeline, 3,5-diaminotriazole, triaminopyrimidine, 2-mercapto-4,6-diaminopyrimidine and carbamoyl triazines of the formula $C_3N_3(NHCOXR)_3$ where X is nitrogen, oxygen or carbon and R is a lower alkyl group having from one to twelve carbon atoms or mixtures of lower alkyl groups, such as methyl, ethyl, propyl, butyl, n-octyl and 2-ethylhexyl. Such compounds and their preparation are described in detail in U.S. Patent No. 5,084,541, which is hereby incorporated by reference.

[0039] The aminoplast resins often contain methylol or similar alkylol groups, and in most instances at least a portion of these alkylol groups are etherified by reaction with an alcohol. Any monohydric alcohol can be employed for this purpose, including methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, as well as benzyl alcohol and other aromatic alcohols, cyclic alcohols such as cyclohexanol, monoethers of glycols, and halogen-substituted or other substituted alcohols such as 3-chloropropanol and butoxyethanol.

[0040] The polyisocyanate which is utilized as a crosslinking agent can be prepared from a variety of isocyanate-containing materials. The polyisocyanate may be a blocked polyisocyanate, or more often is unblocked and the curable film-forming composition is prepared as a two-pack composition, curable at room temperature. Examples of suitable polyisocyanates include trimers prepared from the following diisocyanates: toluene diisocyanate, 4,4'-methylene-bis(cyclohexyl isocyanate), isophorone diisocyanate, an isomeric mixture of 2,2,4- and 2,4,4-trimethyl hexamethylene diisocyanate, 1,6-hexamethylene diisocyanate, tetramethyl xylylene diisocyanate and 4,4'-diphenylmethylene diisocyanate. In addition, blocked polyisocyanate prepolymers of various polyols such as polyester polyols can also be used. Examples of suitable blocking agents include those materials which would unblock at elevated temperatures such as lower aliphatic alcohols including methanol, oximes such as methyl ethyl ketoxime, lactams such as caprolactam and pyrazoles such as dimethyl pyrazole.

[0041] Alternatively, the curing agent (b) comprises a polyisocyanate having free isocyanate functional groups and the curable film-forming composition is a two-package system.

[0042] The polyisocyanate may include a single trifunctional polyisocyanate or a mixture of two or more different trifunctional polyisocyanates, and may be selected from one or more polyisocyanates such as triisocyanates including isocyanurates.

[0043] Suitable trifunctional isocyanates include, but are not limited to, trimers of isophorone diisocyanate, triisocyanato nonane, triphenylmethane triisocyanate, 1,3,5-benzene triisocyanate, 2,4,6-toluene triisocyanate, an adduct of trimethylol and tetramethyl xylene diisocyanate sold under the name CYTHANE 3160 by CYTEC Industries, Inc., DESMODUR N 3300, which is the isocyanurate of hexamethylene diisocyanate, and DESMODUR Z 4470, a trimer of isophorone diisocyanate, both available from Bayer Corporation. Specifically used polyisocyanates are cyclic isocyanates, particularly, isocyanurates of diisocyanates such as hexamethylene diisocyanate and isophorone diisocyanate.

[0044] The polyisocyanate may also be any of those disclosed above, chain extended with one or more polyamines and/or polyols using suitable materials and techniques known to those skilled in the art.

[0045] The amount of the curing agent (b) generally ranges from 10 to 90 percent by weight, or 20 to 80 percent by weight, or 30 to 60 percent by weight, based on the total weight of resin solids (curing agent plus all polymers containing functional groups) in the film-forming composition.

[0046] The curable film-forming compositions of the present invention further comprise (c) silica particles that have been functionalized on their surfaces with an aminosilane so as to impart the surfaces with primary amino functional groups. The silica particles may be fumed silica or precipitated silica. The silica particles may be made from wet processes; such silicas include precipitated silica or gel silica. Alternatively dry or thermal processes may be used to prepare fumed silica, arc silica or plasma silica. Fumed silica may be prepared from flame pyrolysis of silicon tetrachloride. Precipitated silica may be prepared by reacting an alkaline silicate solution with a mineral acid. For example, sulfuric acid and sodium silicate solutions may be added simultaneously to water under agitation. Precipitation is performed under alkaline conditions. The type of agitation, duration of precipitation, the addition rate of reactants, their temperature and concentration, and pH can vary the properties of the final precipitated silica. The formation of a gel stage is avoided by stirring at elevated temperatures. The resulting white precipitate is filtered, washed and dried in the manufacturing process.

[0047] Examples of aminosilanes that may be reacted with the silica to functionalize the surface thereof include aminopropyl trialkoxysilanes such as aminopropyltriethoxysilane, available from Dow Corning as Z-6011.

[0048] The amount of functionalized, silica particles (c) generally ranges from 5 to 25 percent by weight, or 10 to 25 percent by weight, or 15 to 20 percent by weight, based on the total weight of resin solids (curing agent plus all compounds containing functional groups) in the film-forming composition.

[0049] In two-pack compositions, the silica particles are typically included with the polymeric binder (a).

[0050] Other optional ingredients, such as colorants, catalysts, plasticizers, anti-oxidants, thixotropic agents, hindered amine light stabilizers, UV light absorbers and stabilizers may be formulated into the curable compositions of the present invention. These ingredients may be present (on an individual basis) in amounts up to 10 percent, often from 0.1 to 5 percent by weight based on total weight of resin solids of the film-forming composition. When the composition of the present invention includes aminoplast curing agents, catalysts including acid functional catalysts known to those skilled in the art as useful in aminoplast-cured compositions, such as para-toluenesulfonic acid, dodecylbenzene sulfonic acid, and the like, may be included as well.

[0051] The coatings of the present invention can also include a colorant. As used herein, the term “colorant” means any substance that imparts color and/or other opacity and/or other visual effect to the composition. The colorant can be added to the coating in any suitable form, such as discrete particles, dispersions, solutions and/or flakes. A single colorant or a mixture of two or more colorants can be used in the coatings of the present invention.

[0052] Example colorants include pigments, dyes and tints, such as those used in the paint industry and/or listed in the Dry Color Manufacturers Association (DCMA), as well as special effect compositions. A colorant may include, for example, a finely divided solid powder that is insoluble but wettable under the conditions of use. A colorant can be organic or inorganic and can be agglomerated or non-agglomerated. Colorants can be incorporated into the coatings by grinding or simple mixing. Colorants can be incorporated by grinding into the coating by use of a grind vehicle, such as an acrylic grind vehicle, the use of which will be familiar to one skilled in the art.

[0053] Example pigments and/or pigment compositions include, but are not limited to, carbazole dioxazine crude pigment, azo, monoazo, disazo, naphthol AS, salt type (lakes), benzimidazolone, condensation, metal complex, isoindolinone, isoindoline and polycyclic phthalocyanine, quinacridone, perylene, perinone, diketopyrrolo pyrrole, thioindigo, anthraquinone, indanthrone, anthrapyrimidine, flavanthrone, pyranthrone, anthanthrone, dioxazine, triarylcarbonium, quinophthalone pigments, diketo pyrrolo pyrrole red ("DPPBO red"), titanium dioxide, carbon black and mixtures thereof. The terms "pigment" and "colored filler" can be used interchangeably.

[0054] Example dyes include, but are not limited to, those that are solvent and/or aqueous based such as acid dyes, azoic dyes, basic dyes, direct dyes, disperse dyes, reactive dyes, solvent dyes, sulfur dyes, mordant dyes, for example, bismuth vanadate, anthraquinone, perylene, aluminum, quinacridone, thiazole, thiazine, azo, indigoid, nitro, nitroso, oxazine, phthalocyanine, quinoline, stilbene, and triphenyl methane.

[0055] Example tints include, but are not limited to, pigments dispersed in water-based or water miscible carriers such as AQUA-CHEM 896 commercially available from Degussa, Inc., CHARISMA COLORANTS and MAXITONER INDUSTRIAL COLORANTS commercially available from Accurate Dispersions division of Eastman Chemical, Inc.

[0056] As noted above, the colorant can be in the form of a dispersion including, but not limited to, a nanoparticle dispersion. Nanoparticle dispersions can include one or more highly dispersed nanoparticle colorants and/or colorant particles that produce a desired visible color and/or opacity and/or visual effect. Nanoparticle dispersions can include colorants such as pigments or dyes having a particle size of less than 150 nm, such as less than 70 nm, or less than 30 nm. Nanoparticles can be produced by milling stock organic or inorganic pigments with grinding media having a particle size of less than 0.5 mm. Example nanoparticle dispersions and methods for making them are identified in U.S. Patent No. 6,875,800 B2, which is incorporated herein by reference. Nanoparticle dispersions can also be produced by crystallization, precipitation, gas phase condensation, and chemical attrition (i.e., partial dissolution). In order to minimize re-agglomeration of nanoparticles within the coating, a dispersion of resin-coated nanoparticles can be used. As used herein, a "dispersion of resin-coated nanoparticles" refers to a continuous phase in which is dispersed discreet "composite microparticles" that comprise a nanoparticle and a resin coating on the nanoparticle. Example dispersions of resin-coated nanoparticles and methods for making them are identified in U.S. Application No. 10/876,031 filed June 24, 2004, which is incorporated herein by reference, and U.S. Provisional Application No. 60/482,167 filed June 24, 2003, which is also incorporated herein by reference.

[0057] Example special effect compositions that may be used in the coating of the present invention include pigments and/or compositions that produce one or more appearance effects such as reflectance, pearlescence, metallic sheen, phosphorescence, fluorescence, photochromism, photosensitivity, thermochromism, goniochromism and/or color-change. Additional special effect compositions can provide other perceptible properties, such as reflectivity, opacity or texture. In a non-limiting embodiment, special effect compositions can produce a color shift, such that the color of the coating changes when the coating is viewed at different angles. Example color effect compositions are identified in U.S. Patent No. 6,894,086, incorporated herein by reference. Additional color effect compositions can include transparent coated mica and/or synthetic mica, coated silica, coated alumina, a transparent liquid crystal pigment, a liquid crystal coating, and/or any composition wherein interference results from a refractive index differential within the material and not because of the refractive index differential between the surface of the material and the air.

[0058] In certain non-limiting embodiments, a photosensitive composition and/or photochromic composition, which reversibly alters its color when exposed to one or more light sources, can be used in the coating of the present invention. Photochromic and/or photosensitive compositions can be activated by exposure to radiation of a specified wavelength. When the composition becomes excited, the molecular structure is changed and the altered structure exhibits a new color that is different from the original color of the composition. When the exposure to radiation is removed, the photochromic and/or photosensitive composition can return to a state of rest, in which the original color of the composition returns. In one non-limiting embodiment, the photochromic and/or photosensitive composition can be colorless in a non-excited state and exhibit a color in an excited state. Full color-change can appear within milliseconds to several minutes, such as from 20 seconds to 60 seconds. Example photochromic and/or photosensitive compositions include photochromic dyes.

[0059] In a non-limiting embodiment, the photosensitive composition and/or photochromic composition can be associated with and/or at least partially bound to, such as by covalent bonding, a polymer and/or polymeric materials of a polymerizable component. In contrast to some coatings in which the photosensitive composition may migrate out of the coating and crystallize into the substrate, the photosensitive composition and/or photochromic composition associated with and/or at least partially bound to a polymer and/or polymerizable component in accordance with a non-limiting embodiment of the present invention, have minimal migration out of the coating. Example photosensitive compositions and/or photochromic compositions and methods for making them are identified in U.S. Application Serial No. 10/892,919 filed July 16, 2004 and incorporated herein by reference.

[0060] In general, the colorant can be present in the coating composition in any amount sufficient to impart the desired property, visual and/or color effect. The colorant may comprise from 1 to 65 weight percent of the present compositions, such as from 3 to 40 weight percent or 5 to 35 weight percent, with weight percent based on the total weight of the compositions.

[0061] The curable film-forming compositions of the present invention may contain color pigments conventionally used in surface coatings and may be used as matte finish or “low gloss” monocoats; that is, low gloss pigmented coatings. By "low gloss" it is meant that the cured coating has an initial 85° gloss measurement of less than 30, often less than 20, as measured by standard techniques known to those skilled in the art. Such standard techniques include ASTM D523 for gloss measurement.

[0062] The curable film-forming compositions of the present invention may alternatively be used as a matte finish clear coat layer of a multi-layer composite coating composition, such as a color-plus-clear composite coating, as noted below.

[0063] The curable film-forming compositions of the present invention may be curable at ambient temperatures or elevated temperatures, depending on the crosslinking chemistry employed. The film-forming compositions of the present invention are most suitable as topcoats, in particular, clear coats and monocoats, by virtue of their matte finish and burnish-resistant properties as discussed below. The compositions may be easily prepared by simple mixing of the ingredients, using formulation techniques well known in the art.

[0064] The compositions of the present invention may be applied over any of a variety of substrates such as metallic, glass, wood, and/or polymeric substrates, and can be applied by conventional means including but not limited to brushing, dipping, flow coating, spraying and the like. They are most often applied by spraying. The usual spray techniques and equipment for air spraying, airless spraying, and electrostatic spraying employing manual and/or automatic methods can be used. Suitable substrates include but are not limited to metal substrates such as ferrous metals, zinc, copper, magnesium, aluminum, aluminum alloys, and other metal and alloy substrates typically used in the manufacture of automobile and other vehicle bodies. The ferrous metal substrates may include iron, steel, and alloys thereof. Non-limiting examples of useful steel materials include cold rolled steel, galvanized (zinc coated) steel, electrogalvanized steel, stainless steel, pickled steel, zinc-iron alloy such as GALVANNEAL, and combinations thereof. Combinations or composites of ferrous and non-ferrous metals can also be used.

[0065] The compositions of the present invention may also be applied over elastomeric, plastic, or composite substrates such as those that are found on motor vehicles. By "plastic" is meant any of the common thermoplastic or thermosetting synthetic nonconductive materials, including thermoplastic olefins such as polyethylene and polypropylene, thermoplastic urethane, polycarbonate, thermosetting sheet molding compound, reaction-injection molding compound, acrylonitrile-based materials, nylon, and the like. By “composite” is meant any substrate consisting of fibers, typically of glass or carbon, or other filler material that is incorporated with polymeric or plastic materials, commonly of epoxy type polymers.

[0066] The curable film-forming composition of the present invention can be applied to the substrate or on top of a basecoat by any conventional coating technique, including, but not limited to, any of those disclosed above. The transparent topcoat can be applied to a cured or to a dried basecoat before the basecoat has been cured. In the latter instance, the two coatings can then be heated to cure both coating layers simultaneously.

[0067] Where the basecoat is not formed from a composition of the present invention (but the topcoat is formed from a curable coating composition of the present invention) the coating composition of the basecoat in the color-plus-clear system can be any composition useful in coatings applications, particularly automotive applications. The coating composition of the basecoat can comprise a resinous binder and a pigment and/or other colorant, as well as optional additives well known in the art of coating compositions. Nonlimiting examples of resinous binders are acrylic polymers, polyesters, alkyds, and polyurethanes.

[0068] The basecoat compositions can be applied to any of the substrates described above by any conventional coating techniques such as those described above, but are most often applied by spraying. The usual spray techniques and equipment for air spraying, airless spray, and electrostatic spraying employing either manual or automatic methods can be used. Resultant film thicknesses may vary as desired.

[0069] After forming a film of the basecoat on the substrate, the basecoat can be cured or alternatively given a drying step in which at least some of the solvent is driven out of the basecoat film by heating or an air drying period before application of the clearcoat. Suitable drying conditions may depend, for example, on the particular basecoat composition, and on the ambient humidity if the composition is water-borne.

[0070] The transparent or clear topcoat composition can be applied to the basecoat by any conventional coating technique, including, but not limited to, any of those disclosed above. The transparent topcoat can be applied to a cured or to a dried basecoat before the basecoat has been cured. In the latter instance, the two coatings can then be heated to cure both coating layers simultaneously.

[0071] A second topcoat coating composition can be applied to the first topcoat to form a "clear-on-clear" topcoat. The first topcoat coating composition can be applied over the basecoat as described above. The second topcoat coating composition can be applied to a cured or to a dried first topcoat before the basecoat and first topcoat have been cured. The basecoat, the first topcoat and the second topcoat can then be heated to cure the three coatings simultaneously.

[0072] It should be understood that the second transparent topcoat and the first transparent topcoat coating compositions can be the same or different provided that, when applied wet-on-wet, one topcoat does not substantially interfere with the curing of the other, for example, by inhibiting solvent/water evaporation from a lower layer. Moreover, both the first topcoat and the second topcoat can be the curable coating composition of the present invention. Alternatively, only the second topcoat may be formed from the curable coating composition of the present invention.

[0073] If the first topcoat does not comprise the curable coating composition of the present invention, it may, for example, include any crosslinkable coating composition comprising a thermosettable coating material and a curing agent.

[0074] Typically, after forming the first topcoat over the basecoat, the first topcoat is given a drying step in which at least some solvent is driven out of the film by heating or, alternatively, an air drying period or curing step before application of the second topcoat. Suitable drying conditions will depend on the particular film-forming compositions used.

[0075] The film-forming composition of the present invention when employed as a second topcoat coating composition can be applied as was described above for the first topcoat by any conventional coating application technique. Curing conditions can be those described above for the topcoat.

[0076] The curable film-forming compositions of the present invention, after being applied to a substrate as a coating and after curing, demonstrate an initial 85° gloss of less than 30, such as less than 20 or less than 10, and an increase in 85° gloss of no more than 10 gloss units, or no more than 5 gloss units, when subjected to WET ABRASION TEST METHOD ONE. In certain embodiments of the present invention, the curable film-forming compositions will even demonstrate a decrease in gloss after subjection to the abrasion test

[0077] Additionally, in certain embodiments of the present invention, the curable film-forming compositions of the present invention, after being applied to a substrate as a coating and after curing, demonstrate an initial 85° gloss of less than 30, such as less than 20 or less than 10, and an increase in 85° gloss of no more than 15 gloss units, or no more than 10 gloss units, when subjected to WET ABRASION TEST METHOD TWO. In certain embodiments of the present invention, the curable film-forming compositions will even demonstrate a decrease in gloss after subjection to the abrasion test.

[0078] Each of the WET ABRASION TEST METHODS ONE and TWO corresponds, respectively, to the Amtec-Kistler Car Wash Test DIN 55668, run at 10 or 40 cycles, respectively. In the WET ABRASION TESTS ONE and TWO, a cured coating on a substrate is subjected to testing by first measuring the 85° gloss of the coating ("original gloss"). The coating is then subjected to the Amtec-Kistler Car Wash Test DIN 55668, run at 10 or 40 cycles, and afterward, the 85° gloss is again measured.

[0079] The curable film-forming compositions of the present invention, after being applied to a substrate as a coating and after curing, demonstrate an initial 85° gloss of less than 30, such as less than 20 or less than 10, and an increase in 85° gloss of no more than 15 gloss units, or no more than 10 gloss units, when subjected to DRY ABRASION TEST METHOD ONE. Additionally, in certain embodiments of the present invention, the curable film-forming compositions of the present invention, after being applied to a substrate as a coating and after curing, demonstrate an initial 85° gloss of less than 30, such as less than 20 or less than 10, and an increase in 85° gloss of no more than 15 gloss units, or no more than 10 gloss units, when subjected to DRY ABRASION TEST METHOD TWO.

[0080] Each of the DRY ABRASION TEST METHODS ONE and TWO are carried out such that the coating is linearly scratched with a weighted abrasive paper for ten double rubs using an Atlas AATCC CROCKMETER, Model CM-

5, available from Atlas Electric Devices Company of Chicago, Ill. The abrasive paper used is 3M 281Q WETORDRY™ PRODUCTION™ 2 and 9 micron polishing paper sheets for DRY ABRASION TEST METHODS ONE and TWO respectively, which are commercially available from 3M Company of St. Paul, Minn. In the DRY ABRASION TESTS ONE and TWO, a cured coating on a substrate is subjected to testing by first measuring the 85° gloss of the coating ("original gloss"). The coating is then subjected to DRY ABRASION TESTS ONE and TWO, and afterward, the 85° gloss is again measured.

[0081] Given their unique properties, the curable film-forming compositions of the present invention are particularly suitable for use in a method of improving burnish resistance of a substrate in accordance with the present invention. The method comprises: (1) applying to the substrate a curable film-forming composition to form a coated substrate, and (2) (a) heating the coated substrate to a temperature and for a time sufficient to cure the curable film-forming composition or (b) allowing a time sufficient to cure the curable film-forming composition under ambient conditions. The curable film-forming composition comprises any of those described above and forms the outermost layer, or topcoat, on the coated substrate.

[0082] The present invention is more particularly described in the following examples, which are intended to be illustrative only, since numerous modifications and variations therein will be apparent to those skilled in the art. Unless otherwise specified, all parts and percentages are by weight.

Example A

[0083] This example describes the preparation of aminosilane treated silica flatting agent.

[0084] Hi-Sil 2000P, a precipitated silica product (BET surface area of 225 m^2/g) of PPG Industries, was milled and classified to a volume median particle size (measured by Beckman Coulter LS 230 instrument) of 10 micron and a maximum particle size of 22.5 micron. This silica was treated with 16% amino propyl triethoxy silane (Z-6011 by Dow Corning, also called 3-triethoxysilylpropylamine and its chemical formula is $H_2N(CH_2)_3Si(OC_2H_5)_3$) by blending it in a Waring blender continuously with silane pumped at uniform rate for five minutes with a Masterflex pump fitted with Viton tubing. The uniform blend was subjected to 120 degree Celcius for two hours in a convection oven. The silica sample, after amine silane reaction, had 2.3% carbon, 2.1% moisture, 267 ml dibutyl phthalate/100 g oil absorption, 189 m^2/g BET surface area, 10.2 micron volume median particle size.

[0085] Examples 1 and 2 demonstrate the preparation of curable film-forming compositions according to the present invention. The compositions were prepared by first mixing the separate packs of ingredients, and then combining the packs immediately prior to application to the substrates.

Ingredient	Example 1: Weight (g)	Example 2: Weight (g)
A-Pack:		
D8150[1]	42.1	42.1
Amine functional silica[2]	5.06	7.16
D871[1]	18.5	20.0
B-Pack:		
D8371[1]	15.4	15.4

[1] Available from from PPG Industries, Inc.

[2] As described above in Example A

[0086] The film forming compositions of Example 1 and 2 were spray applied to a pigmented basecoat to form color-plus-clear composite coatings over primed electrocoated steel panels. The panels used were ACT cold roll steel panels (10.16 cm by 30.48 cm) with ED6060 electrocoat available from ACT Laboratories, Inc. Separate panels were coated with an ENVIROBASE High Performance (EHP) pigmented water-borne basecoat, available from PPG Industries, Inc. Black EHP T407 was hand sprayed using a SATAjet 3000 with WSB fluid nozzle at ambient temperature (about 70° F. (21° C.)). A dry film thickness of about 0.3 to 0.8 mils (about 7 to 20 micrometers) was targeted for the basecoat. The basecoat panels were allowed to flash at ambient temperature (about 70° F. (21° C.)) for at least 15 minutes prior to clearcoat application.

[0087] The coating compositions were each hand sprayed using a Devilbiss GTi HVLP spray gun to a basecoated panel at ambient temperature in two coats with an ambient flash between applications. Clearcoats were targeted for a 1.5 to 2.5 mils (about 38 to 64 micrometers) dry film thickness. All coatings were allowed to cure at ambient temperature or air flash for about 20 minutes before being baked. The optional bake was for thirty minutes at 140° F. (60° C.). Seven days after clearcoat application, the coated panels were subjected to DRY ABRASION TEST METHOD ONE and TWO and WET ABRASION TEST METHODS ONE and TWO to determine burnish resistance. Table 1 below illustrates the WET ABRASION TEST METHOD results and Table 2 illustrates the DRY ABRASION TEST METHOD results for the curable film-forming composition of Example 1.

Table1

Coating	Original 85° Gloss	Gloss after WET ABRASION TEST METHOD ONE	Gloss after WET ABRASION TEST METHOD TWO
Example 1	13.4	17.8	27
Example 2	5.3	6.7	9.2

Table 2

Coating	Original 85° Gloss	Gloss after DRY ABRASION TEST METHOD ONE	Gloss after DRY ABRASION TEST METHOD TWO
Example 1	13.4	23.9	25.6
Example 2	5.3	11.0	13.6

[0088] Data in the tables indicate that the curable film-forming compositions of the present invention demonstrate excellent burnish resistance. The Example coatings show a gloss increase of less than 5 gloss units for WET ABRASION TEST METHOD ONE. Also, the Example coatings show a gloss increase of 12.2 gloss units or less for DRY ABRASION TEST METHOD TWO.

[0089] The present invention has been described with reference to specific details of particular embodiments thereof. It is not intended that such details be regarded as limitations upon the scope of the invention except insofar as and to the extent that they are included in the accompanying claims.

We claim:

1. A curable film-forming composition comprising:

(a) a polymeric binder comprising at least one polymeric resin having reactive functional groups;

(b) a curing agent containing functional groups that are reactive with the reactive functional groups of (a); and

(c) silica particles that have been functionalized on their surfaces with an amino silane so as to impart the surfaces with primary amino functional groups;

wherein after application to a substrate as a coating and after curing, the curable film-forming composition demonstrates an initial 85° gloss of less than 30 and an increase in 85° gloss of no more than 10 gloss units when subjected to WET ABRASION TEST METHOD ONE.

2. The curable film-forming composition of claim 1 wherein the amino functionalized silica particles are present in the curable film-forming composition in an amount of 5 to 25 percent by weight, based on the total weight of resin solids in the curable film-forming composition.

3. The curable film-forming composition of claim 1, wherein the reactive functional groups of (a) are selected from the group consisting of hydroxyl groups, carbamate groups, carboxyl groups, isocyanate groups, carboxylate groups, primary amine groups, secondary amine groups, amide groups, urea groups, urethane groups, epoxy groups, and combinations thereof.

4. The curable film-forming composition of claim 3, wherein the polymeric binder of (a) comprises at least one hydroxyl functional acrylic and/or polyester polymer.

5. The curable film-forming composition of claim 1, wherein the curing agent of (b) is selected from the group consisting of polyisocyanates, aminoplasts, and combinations thereof.

6. The curable film-forming composition of claim 5, wherein the curing agent of (b) comprises a polyisocyanate having free isocyanate functional groups and the curable film-forming composition is a two-package system, curable at ambient conditions.

7. The curable film-forming composition of claim 6 wherein the curing agent of (b) comprises a mixture polyisocyanates derived from isophorone diisocyanate and hexamethylene diisocyanate.

8. The curable film-forming composition of claim 1 wherein after application to a substrate as a coating and after curing, the curable film-forming composition demonstrates an initial 85° gloss of less than 30 and an increase in 85° gloss of no more than 5 gloss units when subjected to WET ABRASION TEST METHOD ONE.

9. A curable film-forming composition comprising:

(a) a polymeric binder comprising at least one polymeric resin having reactive functional groups;

(b) a curing agent containing functional groups that are reactive with the reactive functional groups of (a); and

(c) silica particles that have been functionalized on their surfaces with an amino silane so as to impart the surfaces with primary amino functional groups;

wherein after application to a substrate as a coating and after curing, the curable film-forming composition demonstrates an initial 85° gloss of less than 30 and an increase in 85° gloss of no more than 15 gloss units when subjected to WET ABRASION TEST METHOD TWO.

10. A multi-component composite coating composition comprising a first film-forming composition applied to a substrate to form a colored base coat, and a second, transparent film-forming composition applied on top of the base coat to form a clear top coat, wherein the transparent film-forming composition comprises a curable film-forming composition comprising:

(a) a polymeric binder comprising at least one polymeric resin having reactive functional groups;

(b) a curing agent containing functional groups that are reactive with the reactive functional groups of (a); and

(c) silica particles that have been functionalized on their surfaces with an amino silane so as to impart the surfaces with primary amino functional groups;

wherein after application to a substrate as a coating and after curing, the curable film-forming composition demonstrates an initial 85° gloss of less than 30 and an increase in 85° gloss of no more than 10 gloss units when subjected to WET ABRASION TEST METHOD ONE.

11. The multi-component composite coating composition of claim 10 wherein the amino functionalized silica particles are present in the curable film-forming composition in an amount of 5 to 25 percent by weight, based on the total weight of resin solids in the curable film-forming composition.

12. The multi-component composite coating composition of claim 10, wherein the reactive functional groups of (a) are selected from the group consisting of hydroxyl groups, carbamate groups, carboxyl groups, isocyanate groups, carboxylate groups, primary amine groups, secondary amine groups, amide groups, urea groups, urethane groups, epoxy groups, and combinations thereof.

13. The multi-component composite coating composition of claim 12, wherein the polymeric binder of (a) comprises at least one hydroxyl functional acrylic and/or polyester polymer.

14. The multi-component composite coating composition of claim 10, wherein the curing agent of (b) is selected from the group consisting of polyisocyanates, aminoplasts, and combinations thereof.

15. The multi-component composite coating composition of claim 14, wherein the curing agent of (b) comprises a polyisocyanate having free

isocyanate functional groups and the curable film-forming composition is a two-package system, curable at ambient conditions.

16. The multi-component composite coating composition of claim 15 wherein the curing agent of (b) comprises a mixture polyisocyanates derived from isophorone diisocyanate and hexamethylene diisocyanate.

17. The multi-component composite coating composition of claim 10 wherein after application to a substrate as a coating and after curing, the curable film-forming composition demonstrates an initial 85° gloss of less than 30 and an increase in 85° gloss of no more than 5 gloss units when subjected to WET ABRASION TEST METHOD ONE.

18. The multi-component composite coating composition of claim 10 wherein after application to a substrate as a coating and after curing, the curable film-forming composition demonstrates an initial 85° gloss of less than 30 and an increase in 85° gloss of no more than 15 gloss units when subjected to WET ABRASION TEST METHOD TWO.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/059209

A. CLASSIFICATION OF SUBJECT MATTER
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ADD.

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	TW I 296 566 B (NIPPON STEEL & SUMIKIN SST [JP]) 11 May 2008 (2008-05-11) the whole document -----	1-18
X	JP 2007 098883 A (NIPPON STEEL & SUMIKIN SST) 19 April 2007 (2007-04-19) the whole document -----	1-18
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer
Glomm, Bernhard

INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 086 974 A1 (WACKER CHEMIE GMBH [DE]) 28 March 2001 (2001-03-28) paragraph [0008] - paragraph [0015] paragraph [0018] - paragraph [0029] paragraph [0034] - paragraph [0044] abstract; claims 1, 2, 8, 16-23; examples 1-3 -----	1-18

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Information on patent family members

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(71) 申请人 PPG 工业俄亥俄公司
地址 美国俄亥俄州

(72) 发明人 S·J·莫拉维克 S·莫纳特
S·J·托马斯

(74) 专利代理机构 中国国际贸易促进委员会专利商标事务所 11038
代理人 孙悦

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(54) 发明名称

显示出耐抛光性和低光泽度的能固化成膜组合物

(57) 摘要

本发明涉及能固化成膜组合物，包含：(a) 包含至少一种聚合物型树脂的聚合物型粘合剂，所述聚合物型树脂具有反应性官能团；(b) 含有与 (a) 的反应性官能团有反应性的官能团的固化剂；以及 (c) 二氧化硅颗粒，用氨基硅烷在它们的表面上官能化以便将伯氨基官能团赋予所述表面。在作为涂料施涂于基材之后并且在固化之后，当经受如本文所限定的各种磨损测试方法时，所述能固化成膜组合物显示出小于 30 的初始 85° 光泽度以及不大于 15 光泽度单位的 85° 光泽度的增加。

1. 能固化成膜组合物，包含：

(a) 包含至少一种聚合物型树脂的聚合物型粘合剂，所述聚合物型树脂具有反应性官能团；

(b) 含与 (a) 的反应性官能团有反应性的官能团的固化剂；以及

(c) 二氧化硅颗粒，所述二氧化硅颗粒已用氨基硅烷在它们的表面上官能化从而将伯氨基官能团赋予所述表面；

其中在作为涂料施涂于基材之后并且在固化之后，当经受湿磨测试方法一时，所述能固化成膜组合物显示出小于30个光泽度单位的初始85° 光泽度以及不大于10个光泽度单位的85° 光泽度的增加。

2. 权利要求 1 所述的能固化成膜组合物，其中所述氨基官能化二氧化硅颗粒基于所述能固化成膜组合物中树脂固体的总重量计以 5-25 重量％的量存在于所述能固化成膜组合物中。

3. 权利要求 1 所述的能固化成膜组合物，其中 (a) 的反应性官能团选自羟基、氨基甲酸酯基、羧基、异氰酸酯基、羧酸酯基、伯胺基、仲胺基、酰胺基、脲基、氨基甲酸酯基、环氧基、及其组合。

4. 权利要求 3 所述的能固化成膜组合物，其中 (a) 的聚合物型粘合剂包含至少一种羟基官能丙烯酸类和 / 或聚酯类聚合物。

5. 权利要求 1 所述的能固化成膜组合物，其中 (b) 的固化剂选自多异氰酸酯、氨基塑料、及其组合。

6. 权利要求 5 所述的能固化成膜组合物，其中 (b) 的固化剂包含具有游离异氰酸酯官能团的多异氰酸酯并且所述能固化成膜组合物是双组分系统，在环境条件下能固化。

7. 权利要求 6 所述的能固化成膜组合物，其中 (b) 的固化剂包含得自异佛尔酮二异氰酸酯和六亚甲基二异氰酸酯的多异氰酸酯混合物。

8. 权利要求 1 所述的能固化成膜组合物，其中在作为涂料施涂于基材之后并且在固化之后，当经受湿磨测试方法一时，所述能固化成膜组合物显示出小于 30 个光泽度单位的初始 85° 光泽度以及不大于 5 个光泽度单位的 85° 光泽度的增加。

9. 能固化成膜组合物，包含：

(a) 包含至少一种聚合物型树脂的聚合物型粘合剂，所述聚合物型树脂具有反应性官能团；

(b) 含有与 (a) 的反应性官能团有反应性的官能团的固化剂；以及

(c) 二氧化硅颗粒，所述二氧化硅颗粒已用氨基硅烷在它们的表面上官能化从而将伯氨基官能团赋予所述表面；

其中在作为涂料施涂于基材之后并且在固化之后，当经受湿磨测试方法二时，所述能固化成膜组合物显示出小于30个光泽度单位的初始85° 光泽度以及不大于15个光泽度单位的85° 光泽度的增加。

10. 多组分复合涂料组合物，包含施涂于基材以形成着色的底漆的第一成膜组合物，和施涂于该底漆之上以形成透明面漆的第二透明成膜组合物，其中所述透明成膜组合物包含能固化成膜组合物，所述能固化成膜组合物包含：

(a) 包含至少一种聚合物型树脂的聚合物型粘合剂，所述聚合物型树脂具有反应性官

能团；

(b) 含有与 (a) 的反应性官能团有反应性的官能团的固化剂；以及

(c) 二氧化硅颗粒，所述二氧化硅颗粒已用氨基硅烷在它们的表面上官能化从而将伯氨基官能团赋予所述表面；

其中在作为涂料施涂于基材之后并且在固化之后，当经受湿磨测试方法一时，所述能固化成膜组合物显示出小于30个光泽度单位的初始85° 光泽度以及不大于10个光泽度单位的85° 光泽度的增加。

11. 权利要求10所述的多组分复合涂料组合物，其中所述氨基官能化二氧化硅颗粒基于所述能固化成膜组合物中树脂固体的总重量计以5-25重量%的量存在于所述能固化成膜组合物中。

12. 权利要求10所述的多组分复合涂料组合物，其中 (a) 的反应性官能团选自羟基、氨基甲酸酯基、羧基、异氰酸酯基、羧酸酯基、伯胺基、仲胺基、酰胺基、脲基、氨基甲酸酯基、环氧基、及其组合。

13. 权利要求12所述的多组分复合涂料组合物，其中 (a) 的聚合物型粘合剂包含至少一种羟基官能丙稀酸类和／或聚酯类聚合物。

14. 权利要求10所述的多组分复合涂料组合物，其中 (b) 的固化剂选自多异氰酸酯、氨基塑料、及其组合。

15. 权利要求14所述的多组分复合涂料组合物，其中 (b) 的固化剂包含具有游离异氰酸酯官能团的多异氰酸酯并且所述能固化成膜组合物是双组分系统，在环境条件下能固化。

16. 权利要求15所述的多组分复合涂料组合物，其中 (b) 的固化剂包含得自异佛尔酮二异氰酸酯和六亚甲基二异氰酸酯的多异氰酸酯混合物。

17. 权利要求10所述的多组分复合涂料组合物，其中在作为涂料施涂于基材之后并且在固化之后，当经受湿磨测试方法一时，所述能固化成膜组合物显示出小于30个光泽度单位的初始85° 光泽度以及不大于5个光泽度单位的85° 光泽度的增加。

18. 权利要求10所述的多组分复合涂料组合物，其中在作为涂料施涂于基材之后并且在固化之后，当经受湿磨测试方法二时，所述能固化成膜组合物显示出小于30个光泽度单位的初始85° 光泽度以及不大于15个光泽度单位的85° 光泽度的增加。

显示出耐抛光性和低光泽度的能固化成膜组合物

发明领域

[0001]　本发明大体涉及显示出耐抛光性和低光泽度性质的能固化成膜组合物。

[0002]　发明背景

[0003]　最近，在涂料工业中，大量的研究工作集中在透明涂层的耐擦伤性和耐磨性。虽然这两种术语经常互换地使用，但是物理和机械结果是非常不同的。刮伤是牵涉小刮擦，通常没有显著移除材料的近表面现象。磨损牵涉更加严重的损害并且经常导致涂层材料的显著损失。由此，耐刮伤性主要受表面性质的影响，而耐磨性受体积性质控制。影响这些机械性质的化学属性经常是不同的。例如，丙烯酸类聚氨酯清漆可具有优良的耐磨性，但是耐刮伤性差。在另一方面，丙烯酸类三聚氰胺涂层可具有良好的耐刮伤性以及平均至差的耐磨性。刮伤损害的一个通常的例子是汽车面漆的光泽损失。新车的高光泽面漆随着时间变得阴暗和模糊，这是由细刮擦和磨损引起的。大部分这样的损害是由在自动洗车中使用的织物或鬃丝的擦洗动作造成的。磨损损害在地面涂层中更常见，并且在其最严重的形式下，基材可变得暴露。高度着色涂料的抛光在文献中的限定较不明确，但是含有刮擦和磨损以及界面粘附的要素。存在至少四种不同的磨损机理在含填料或颜料的涂层中可有助于抛光。1) 在空气 / 表面界面除去膜，2) 通过粘附 (cohesive) 粘合剂失效移除填料，3) 通过粘附失效移除填料和 / 或 4) 填料磨损。哪种机理占优势可取决于涂层、磨损条件和户外暴露而变化。理想地，耐抛光性涂层具有良好的耐磨性，良好的耐刮伤性，和与粘合剂具有优良相容性的颜料颗粒。

[0004]　伪装飞行器典型地使用低光泽度着色涂料以实现许多它们的性能要求。这些低光泽或无光泽面漆表现出物理上的粗糙表面，其，理想地，扩散地反射可见光。这些物理上的粗糙表面难以清洁并且经常需要用研磨垫擦洗，其随着时间的推移可增加涂层反射（称作抛光）的一致性。反射的增加被目视地察觉为导致形成较高对比度的区域的色移。机械地，光泽的这种增加或抛光是由粗糙涂漆表面的磨损产生较光滑的表面（具有更均匀的反射）而造成的。

[0005]　期望开发可重复地用洗涤剂和研磨剂清洁而不增加涂层反射性的能固化成膜组合物。

[0006]　发明概述

[0007]　本发明涉及能固化成膜组合物，包含：

[0008]　(a) 包含至少一种聚合物型树脂的聚合物型粘合剂，所述聚合物型树脂具有反应性官能团；

[0009]　(b) 含与 (a) 的反应性官能团有反应性的官能团的固化剂；以及

[0010]　(c) 二氧化硅颗粒，用氨基硅烷在它们的表面上官能化以便将伯氨基官能团赋予所述表面。在作为涂料施涂于基材之后并且在固化之后，当经受如本文所限定的各种磨损测试方法时，所述能固化成膜组合物显示出小于 30 的初始 85° 光泽度以及不大于 10 光泽度单位的 85° 光泽度的增加。

[0011]　发明的详细说明

[0012] 应注意，除非明确或毫无疑问地限制为一个指示对象，本说明书和所附权利要求中所使用的单数形式“一个”、“一种”和“该”包括复数指示对象。

[0013] 除了在任何操作实施例中，或其中另有说明，否则指代在说明书和权利要求中的成分用量／反应条件等的全部数值或短语应理解为在所有情况下被术语“约”修饰。各种数值范围公开在该专利申请中。因为这些范围是连续的，它们包括在最小和最大值之间的每一个值。除非另有明确说明，在该申请中说明的各种数值范围是约数。

[0014] 关于本发明的范围，本文呈现的本发明的各种实施方式和实施例各自被理解为是非限制性的。

[0015] 以下说明书和权利要求中使用的以下术语具有以下指示的意义：

[0016] 除非另有明确说明，术语“丙烯酸类”和“丙烯酸酯”是互换地使用的（除非这样做会改变所意指的意义）并且包括丙烯酸、丙烯酸酐、及其衍生物，例如它们的 C1-C5 烷基酯、低级烷基－取代的丙烯酸，例如，C1-C5 取代的丙烯酸，例如甲基丙烯酸、乙基丙烯酸等，以及它们的 C1-C5 烷基酯。术语“（甲基）丙烯酸”或“（甲基）丙烯酸酯”意指覆盖所指材料的丙烯酸／丙烯酸酯和甲基丙烯酸／甲基丙烯酸酯形式，例如，（甲基）丙烯酸酯单体。

[0017] 例如与能固化组合物相关联使用的术语“能固化”，是指所指的组合物通过官能团（例如，通过包括但不限于，热（包括常温固化）和／或催化暴露的方式）是能聚合或能交联的。

[0018] 与固化的或能固化组合物相关联使用的术语“固化”，“固化的”或类似的术语，例如，一些具体描述中的“固化的组合物”，是指形成能固化组合物的至少一部分能聚合和／或能交联的组分是聚合和／或交联的。另外地，能聚合组合物的固化是指使所述组合物经受固化条件例如但不限于热固化，导致组合物的反应性官能团的反应，并且导致聚合和聚合产物的形成。当使能聚合组合物经受固化条件时，在聚合之后以及在多数反应性端基发生反应之后，剩余未反应的反应性端基的反应速率逐渐变得更慢。能聚合组合物可经受固化条件直到其至少部分固化。术语“至少部分固化”是指使能聚合组合物经受固化条件，其中组合物的至少一部分反应性基团发生反应，以形成聚合产物。能聚合组合物还可经受固化条件，以使得实现基本上完全固化并且其中进一步固化导致聚合物性质（例如硬度）没有显著的进一步改进。

[0019] 术语“反应性”是指官能团能够自发地或在施加热之后或在催化剂存在下或通过本领域技术人员已知的任何其它方式与其本身和／或其它官能团进行化学反应。

[0020] 术语“耐抛光性”是指涂层在用研磨材料或垫擦洗之后保持其光泽度而不显示出光泽度的显著的增加（即，小于 15 点）的能力。

[0021] 本发明涉及能固化成膜组合物。所述成膜组合物包含 (a) 包含至少一种聚合物型树脂的聚合物型粘合剂，所述聚合性树脂具有反应性官能团。反应性官能团的例子包括羟基、氨基甲酸酯基 (carbamate groups)、羧基、异氰酸酯基、羧酸酯基、伯胺基、仲胺基、酰胺基、脲基、氨基甲酸酯基 (urethane groups)、环氧基、及其组合。

[0022] 适用作合型粘合剂 (a) 的特别有用的聚合物型成膜树脂是丙烯酸类聚合物、聚酯，包括醇酸、和聚氨酯。通常这些聚合物可以是通过本领域技术人员已知的任何方式制备的这些类型的任何聚合物，其中所述聚合物是水可分散性或可乳化的并且优选有限的水溶性。

[0023] 合适的丙烯酸类聚合物包括丙烯酸或甲基丙烯酸的一种或多种烷基酯，任选地连同一种或多种其它能聚合烯属不饱和单体的共聚物。有用的丙烯酸或甲基丙烯酸的烷基酯包括在烷基中含1-30，并且优选4-18个碳原子的脂族烷基酯。非限制性的例子包括甲基丙烯酸甲酯、甲基丙烯酸乙酯、甲基丙烯酸丁酯、丙烯酸乙酯、丙烯酸丁酯、和丙烯酸2-乙基己基酯。合适的其它能共聚合的烯属不饱和单体包括乙烯基芳族化合物例如苯乙烯和乙烯基甲苯；腈类例如丙烯腈和甲基丙烯腈；乙烯基和亚乙烯基卤化物例如乙烯基氯化物和亚乙烯基氟化物，和乙烯基酯例如乙酸乙烯酯。

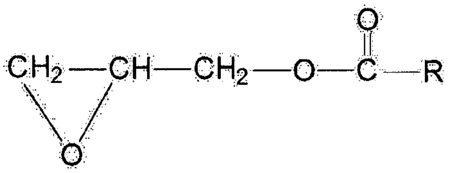
[0024] 丙烯酸类共聚物可包括羟基官能团，其经常通过在用于生产共聚物的反应物中包括一种或多种羟基官能单体而并入聚合物中。有用的羟基官能单体包括典型地在羟烷基中具有2-4个碳原子的丙烯酸羟烷酯和甲基丙烯酸羟烷酯，例如丙烯酸羟乙酯、丙烯酸羟丙酯、丙烯酸4-羟丁酯、己内酯和丙烯酸羟烷酯的羟基官能加合物，和相应的甲基丙烯酸酯，以及下述的β-羟基酯官能单体。丙烯酸类聚合物还可以用N-（烷氧基甲基）丙烯酰胺和N-（烷氧基甲基）甲基丙烯酰胺来制备。

[0025] β-羟基酯官能单体可以用烯属不饱和环氧官能单体和具有约13-约20个碳原子的羧酸来制备，或用烯属不饱和酸官能单体和含至少5个碳原子的环氧化合物来制备，所述环氧化合物不能与烯属不饱和酸官能单体聚合。

[0026] 用于制备β-羟基酯官能单体的有用的烯属不饱和环氧官能单体包括但不限于，丙烯酸缩水甘油酯、甲基丙烯酸缩水甘油酯、烯丙基缩水醚、甲代烯丙基缩水醚、烯属不饱和单异氰酸酯与羟基官能单环氧化物（例如缩水甘油）的1：1（摩尔）加合物、和能聚合多羧酸（例如马来酸）的缩水甘油酯。丙烯酸缩水甘油酯和甲基丙烯酸缩水甘油酯是优选的。羧酸的例子包括但不限于，饱和单羧酸例如异硬脂酸和芳族不饱和羧酸。

[0027] 用于制备β-羟基酯官能单体的有用的烯属不饱和酸官能单体包括单羧酸例如丙烯酸、甲基丙烯酸、巴豆酸；二羧酸例如衣康酸、马来酸和富马酸；以及二羧酸的单酯例如马来酸单丁酯和衣康酸单丁酯。烯属不饱和酸官能单体和环氧化合物典型地以1：1当量比反应。环氧化合物不含有与不饱和酸官能单体参与自由基引发聚合的烯属不饱和基团。有用的环氧化合物包括1，2-环氧戊烷，氧化苯乙烯和缩水甘油酯或缩水甘油醚，优选含8-30个碳原子，例如丁基缩水甘油醚、辛基缩水甘油醚、苯基缩水甘油醚和对-（叔丁基）苯基缩水甘油醚。优选的缩水甘油酯包括具有以下结构的那些：

[0028]



[0029] 其中R是含约4-约26个碳原子的烃基。优选地，R是具有约8-约10个碳原子的支化的烃基，例如新戊酸酯、新庚酸酯或新癸酸酯。合适的羧酸的缩水甘油酯包括VERSATIC ACID 911和CARDURA E，其各自商购自Shell Chemical Co。

[0030] 通过共聚合丙烯酸类单体与氨基甲酸酯官能乙烯基单体（例如甲基丙烯酸的氨基甲酸酯官能烷基酯），或通过将羟基官能丙烯酸类聚合物与低分子量氨基甲酸酯官能材料（例如可经由转氨甲酰化(transcarbamoylation)反应得自醇或二醇醚）反应，可将氨

基甲酸酯官能团可包括在丙烯酸类聚合物中。备选地，可通过将羟基官能丙烯酸类聚合物与低分子量氨基甲酸酯官能材料（例如可经由转氨甲酰化反应得自醇或二醇醚）反应，将氨基甲酸酯官能度引入至丙烯酸类聚合物中。在该反应中，将得自醇或二醇醚的低分子量氨基甲酸酯官能材料与丙烯酸类多元醇的羟基反应，产生氨基甲酸酯官能丙烯酸类聚合物和原始醇或二醇醚。得自醇或二醇醚的低分子量氨基甲酸酯官能材料可在催化剂存在下通过将醇或二醇醚与脲反应来制备。合适的醇包括低分子量脂族、环脂族、和芳族醇例如甲醇、乙醇、丙醇、丁醇、环己醇、2-乙基己醇、和3-甲基丁醇。合适的二醇醚包括乙二醇甲醚和丙二醇甲醚。丙二醇甲醚和甲醇是最经常使用的。其它有用的氨基甲酸酯官能单体公开在美国专利号5,098,947中，其通过引用并入本文。其它有用的氨基甲酸酯官能单体公开在美国专利号5,098,947，其通过引用并入本文。

[0031] 可在聚合物的制备中通过使用合适的官能单体，或通过使用本领域技术人员已知的技术将其它官能团转化成酰胺基，将酰胺官能度引入至丙烯酸类聚合物。同样地，如果期望的话，可使用合适的官能单体（如果有的话）或转化反应（如果必要的话）引入其它官能团。

[0032] 丙烯酸类聚合物可经由水乳液聚合技术来制备并且直接用在水性涂料组合物的制备中，或可以用能够成盐的基团（例如酸或胺基）经由有机溶液聚合技术来制备。在这些基团与碱或酸中和之后，可将聚合物分散在水介质中。通常，可以采用本领域技术人员已知的使用本领域认知量的单体来生产这种聚合物的任何方法。

[0033] 在本发明的特定实施方式中，聚合物型粘合剂(a)包含两种羟基官能丙烯酸类聚合物的混合物。第一种包含苯乙烯、丙烯酸羟丙酯、异硬脂酸、缩水甘油甲基丙烯酸酯、和甲基丙烯酸甲酯的聚合产物，如US5,869,566，实施例1-16中所述，其通过引用并入本文，而第二种包含甲基丙烯酸羟丙酯、甲基丙烯酸甲酯、丙烯酸正丁酯、苯乙烯、CarduraE/丙烯酸加合物、和丙烯酸的聚合产物，根据US6,458,885，其通过引用并入本文并且所述两种聚合物分别以范围为1:1-3:1的重量比混合。

[0034] 除丙烯酸类聚合物之外，在涂料组合物中适合作为聚合物型粘合剂(a)的聚合物型成膜树脂可以是醇酸树脂或聚酯。这种聚合物可以以已知的方式通过多元醇和多羧酸的缩合来制备。合适的多元醇包括但不限于，乙二醇、丙二醇、丁二醇、1,6-己二醇、新戊二醇、二乙二醇、甘油、三羟甲基丙烷、和季戊四醇。合适的多羧酸包括但不限于，琥珀酸、己二酸、壬二酸、癸二酸、马来酸、富马酸、苯二甲酸、四氢苯二甲酸、六氢苯二甲酸、和偏苯三酸。除了上述的多羧酸之外，可以使用酸的官能等价物（例如其中它们存在的酸酐）或酸的低级烷基酯（例如甲酯）。

[0035] 有用的醇酸树脂包括多羟基醇和多羧酸的聚酯，其化学地与不同比例的各种干性、半干性和非干性油结合。因此，例如，醇酸树脂由多羧酸（例如苯二甲酸、马来酸、富马酸、异苯二甲酸、琥珀酸、己二酸、壬二酸、癸二酸）以及由其中它们存在的这些酸的酸酐制备。可以与多羧酸反应的多元醇包括1,4-丁二醇、1,6-己二醇、新戊二醇、乙二醇、二乙二醇和2,3-丁二醇、甘油、三羟甲基丙烷、季戊四醇、山梨醇和甘露醇。

[0036] 通过将多羧酸与多元醇连同的干性、半干性或非干性油（以取决于期望的性质的比例）反应来生产醇酸树脂。该油料在制造期间通过酯化偶联至(coupled into)树脂分子中并且变为聚合物的必要部分。该油料是完全饱和的或大部分不饱和的。当浇筑成膜时，

完全饱和的油料倾向于将增塑效果给予该膜，而大部分不饱和的油料倾向于随着氧化快速交联和干燥以给出更牢固和耐溶剂性的膜。合适的油料包括椰油、鱼油、亚麻籽油、桐油、蓖麻油、棉花籽油、红花油、豆油和妥尔油。使用各种比例的多羧酸、多元醇和油以获得各种性质的醇酸树脂，这是本领域周知的。

[0037] 通过首先形成氨基甲酸羟烷酯（其可以与用于形成聚酯的多元酸和多元醇反应）可将氨基甲酸酯官能团引入至聚酯中。氨基甲酸羟烷酯与聚酯上的酸官能度缩合，产生端基氨基甲酸酯官能度。可经由转氨甲酰化工艺（类似于上述与将氨基甲酸酯基引入至丙烯酸类聚合物中相关的转氨甲酰化）通过将聚酯上的端羟基与低分子量氨基甲酸酯官能材料反应或通过将异氰酸与羟基官能聚酯反应，将氨基甲酸酯官能团引入至聚酯中。

[0038] 如果期望的话，可使用合适的官能反应物（如果有的话），或必要时转化反应以产生期望的官能团而将其它官能团（例如酰胺、硫醇、脲、和硫代氨基甲酸酯）引入至聚酯或醇酸树脂中。这种技术是本领域人员已知的。

[0039] 聚氨酯还可用作本发明成膜组合物中的聚合物型粘合剂 (a)。在其中可以使用的聚氨酯是聚合物型多元醇，其通常通过将聚酯多元醇或丙烯酸类多元醇（例如以上提到的那些）与多异氰酸酯反应（以使得 OH/NCO 当量比大于 1 :1，从而游离羟基存在于产物中）来制备。用于制备聚氨酯多元醇的有机多异氰酸酯可以是脂族或芳族多异氰酸酯或所述两者的混合物。二异氰酸酯是优选的，但是高级多异氰酸酯可以取代二异氰酸酯来使用或与二异氰酸酯结合使用。合适的芳族二异氰酸酯的例子是 4,4'- 二苯基甲烷二异氰酸酯和甲苯二异氰酸酯。合适的脂族二异氰酸酯的例子是直链脂族二异氰酸酯例如 1,6- 六亚甲基二异氰酸酯。同样地，可以采用环脂族二异氰酸酯。例子包括异佛尔酮二异氰酸酯和 4,4'- 亚甲基 - 双 -(环己基异氰酸酯)。合适的高级多异氰酸酯的例子是 1,2,4- 苯三异氰酸酯和多亚甲基多苯基异氰酸酯。关于聚酯，聚氨酯可以用未反应的羧酸基团（其在用碱（例如胺）中和之后能分散到水介质中）来制备。

[0040] 通过将多异氰酸酯与含端基 / 侧基氨基甲酸酯基的聚合物型多元醇反应可将端基和 / 或侧基氨基甲酸酯官能团引入至聚氨酯中。备选地，通过将多异氰酸酯与多元醇和氨基甲酸羟烷酯或异氰酸（作为分别的反应物）反应可将氨基甲酸酯官能团引入聚氨酯中。还可经由转氨甲酰化工艺（类似于上述与将氨基甲酸酯基引入至丙烯酸类聚合物中相关的转氨甲酰化）通过将羟基官能聚氨酯与低分子量氨基甲酸酯官能材料反应将氨基甲酸酯官能团引入至聚氨酯中。另外地，异氰酸酯官能聚氨酯可以与氨基甲酸羟烷酯反应以产生氨基甲酸酯官能聚氨酯。

[0041] 如果期望的话，可使用合适的官能反应物（如果有的话），或必要时转化反应以产生期望的官能团而将其它官能团（例如酰胺、硫醇、脲、和硫代氨基甲酸酯）引入至聚氨酯中。这种技术是本领域人员已知的。

[0042] 存在于聚合物型粘合剂 (a) 中的聚合物的量基于所述成膜组合物中树脂固体的总重量（固化剂加上所有的含官能团聚合物）计通常范围为 10-90 重量%，例如 20-80 重量%，或 40-60 重量%。

[0043] 本发明的能固化成膜组合物进一步包含固化剂 (b)，其包含与 (a) 的反应性官能团有反应性的官能团。固化剂 (b) 可选自，例如，多异氰酸酯和氨基塑料。还可以使用固化剂的混合物。

[0044] 有用的氨基塑料树脂基于甲醛与带有氨基－或酰胺基－的物质的加成产物。由醇和甲醛与三聚氰胺、脲或苯并胍胺的反应获得的缩合产物是本文最常见和优选的。虽然采用的醛最经常是甲醛，其它类似的缩合产物可由其它醛，例如乙醛、丁烯醛、丙烯醛、苯甲醛、糠醛、乙二醛等来制备。

[0045] 还可以使用其它胺类和酰胺类的缩合产物，例如，三嗪、二嗪、三唑、胍、胍胺的醛缩合物以及这些化合物的烷基－和芳基－取代的衍生物（包括烷基－和芳基－取代的脲以及烷基－和芳基－取代的三聚氰胺）。这些化合物的非限制性的例子包括 N,N'－二甲基脲、苯并脲 (bezourea)、双氰胺、甲酰胍胺 (formaguanamine)、乙酰胍胺、甘脲、三聚氰胺二酰胺、3,5- 二氨基三唑、三氨基嘧啶、2- 巯基 -4,6- 二氨基嘧啶和式 $C_3N_3(NHCOXR)_3$的氨基甲酰基三嗪，其中 X 是氮、氧或碳以及 R 是具有 1-12 个碳原子或低级烷基的低级烷基（例如甲基、乙基、丙基、丁基、正辛基和 2- 乙基己基）的混合物。这种化合物和它们的制备详细地描述在美国专利号 5,084,541 中，其以此通过引用并入。

[0046] 氨基塑料树脂经常含有羟甲基或类似的羟烷基，并且在多数情况下这些羟烷基的至少一部分通过与醇反应而醚化。为了该目的可以采用任何一元醇，包括甲醇、乙醇、丙醇、丁醇、戊醇、己醇、庚醇、以及卞醇和其它芳族醇，环醇例如环己醇，二醇的单醚，以及卤素－取代的或其它取代的醇例如 3- 氯丙醇和丁氧基乙醇。

[0047] 用作交联剂的多异氰酸酯可以用各种含异氰酸酯的材料来制备。多异氰酸酯可以是封闭的多异氰酸酯，或更经常是未封闭的并且能固化成膜组合物被制备成双组分组合物，在室温下能固化。合适的多异氰酸酯的例子包括由以下二异氰酸酯制备的三聚物：甲苯二异氰酸酯、4,4'－亚甲基－双（环己基异氰酸酯）、异佛尔酮二异氰酸酯、2,2,4- 和 2,4,4- 三甲基六亚甲基二异氰酸酯的异构体混合物、1,6- 六亚甲基二异氰酸酯、四甲基苯二甲基二异氰酸酯和 4,4'－苯苯基亚甲基二异氰酸酯。此外，还可以使用各种多元醇的封闭的多异氰酸酯预聚物（例如聚酯多元醇）。合适的封闭剂的例子包括在升高的温度下将去封闭的那些材料，例如低级脂族醇包括甲醇，肟例如甲基乙基酮肟，内酰胺例如己内酰胺和吡唑例如二甲基吡唑。

[0048] 备选地，固化剂 (b) 包含具有游离异氰酸酯官能团的多异氰酸酯并且能固化成膜组合物是双组分系统。

[0049] 多异氰酸酯可包括单个的三官能多异氰酸酯或两种或更多种不同的三官能多异氰酸酯的混合物，以及可选自一种或多种多异氰酸酯，例如三异氰酸酯，包括异氰脲酸酯。

[0050] 合适的三官能异氰酸酯包括但不限于，异佛尔酮二异氰酸酯、三异氰酸基壬烷、三苯基甲烷三异氰酸酯的三聚物，1,3,5- 苯三异氰酸酯，2,4,6- 甲苯三异氰酸酯，三羟甲基和四甲基苯二甲基二异氰酸酯的加合物（由 CYTEC Industries,Inc. 以名称 CYTHANE 3160 出售），DESMODUR N 3300，其是六亚甲基二异氰酸酯的异氰脲酸酯，和 DESMODUR Z 4470，其异佛尔酮二异氰酸酯的三聚物，均得自 BayerCorporation。特别使用的多异氰酸酯是环异氰酸酯，特别是，二异氰酸酯（例如六亚甲基二异氰酸酯和异佛尔酮二异氰酸酯）的异氰脲酸酯。

[0051] 多异氰酸酯还可以是任意以上公开的那些，其使用合适的材料和技术用本领域技术人员已知的一种或多种多胺和／或多元醇来链增长。

[0052] 固化剂 (b) 的量的范围基于所述成膜组合物中的树脂固体的总重量计（固化剂加

上所有的含官能团聚合物）通常为 10-90 重量%，或 20-80 重量%，或 30-60 重量%。

[0053] 本发明的能固化成膜组合物进一步包含 (c) 二氧化硅颗粒，用氨基硅烷在它们的表面上官能化以便将伯氨基官能团赋予所述表面。该二氧化硅颗粒可以是锻制二氧化硅或沉淀二氧化硅。该二氧化硅颗粒可以由湿法制备；这种二氧化硅包括沉淀二氧化硅或凝胶状二氧化硅 (gel silica)。备选地，干燥或热工艺可用于制备锻制二氧化硅，电弧二氧化硅 (arc silica) 或等离子体二氧化硅。锻制二氧化硅可以由四氯化硅的火焰裂解 (flame pyrolysis) 制备。沉淀二氧化硅可通过将碱性硅酸盐溶液与无机酸反应来制备。例如，硫酸和硅酸钠溶液可在搅拌的同时添加到水中。沉淀在碱性条件下进行。搅拌的类型、沉淀的时间、反应物的添加速率、它们的温度和浓度，以及 pH 可改变最终沉淀二氧化硅的性质。通过在升高的温度下搅拌来避免形成凝胶状态。得到的白色沉淀在制造过程中过滤、洗涤以及干燥。

[0054] 可以与二氧化硅反应以官能化其表面的氨基硅烷的例子包括氨基丙基三烷氧基硅烷例如氨基丙基三乙氧基硅烷，其作为 Z-6011 得自 Dow Corning。

[0055] 官能化二氧化硅颗粒 (c) 的量基于所述成膜组合物中树脂固体的总重量（固化剂加上所有的含官能团化合物）计的范围通常为 5-25 重量%，或 10-25 重量%，或 15-20 重量%。

[0056] 在双组分组合物中，典型地包括二氧化硅颗粒和聚合物型粘合剂 (a)。

[0057] 其它任选的成分，例如着色剂、催化剂、增塑剂、抗氧化剂、触变剂、受阻胺光稳定剂、紫外光吸收剂和稳定剂可配制成本发明的能固化组合物。这些成分基于所述成膜组合物的树脂固体的总重量计可以以（以单个为基础）至多 10%，经常 0.1-5 重量%的量存在。当本发明的组合物包括氨基塑料固化剂时，还可以包括这样的催化剂，其包括本领域技术人员已知的可用于氨基塑料－固化组合物的酸官能催化剂，例如对－甲苯磺酸，十二烷基苯磺酸等。

[0058] 本发明的涂料还可包括着色剂。本文使用的术语“着色剂”是指将颜色和／或其它不透明性和／或其它目视效果赋予组合物的任何物质。着色剂可以以任何合适的形式（例如分散的颗粒、分散体、溶液和／或片状）添加至涂料。单一着色剂或两种或更多种着色剂的混合物可用在本发明的涂料中。

[0059] 着色剂的例子包括颜料、染料和染料剂，例如用于涂料工业和／或列于 Dry Color Manufacturers Associat ion(DCMA)，以及特殊效果组合物中的那些。着色剂可包括，例如，在使用条件下不可溶但可湿的细分的固体粉末。着色剂可以是有机或无机的并且可以是团聚的或非团聚的。可通过研磨或简单混合将着色剂引入到涂料中。可通过使用研磨工具 (grind vehicle)（例如丙烯酸类研磨工具）研磨将着色剂引入到涂料中，研磨工具的使用对于本领域技术人员来说是熟悉的。

[0060] 颜料和／或颜料组合物的例子包括，但不限于，咔唑二噁嗪天然颜料、偶氮、单偶氮、双偶氮、萘酚 AS、盐型（色淀）、苯并咪唑酮、缩合物、金属络合物、异吲哚酮、异吲哚啉和多环酞菁、喹吖啶酮、二萘嵌苯、紫环酮、二酮吡咯并吡咯、硫靛、蒽醌、靛蒽醌、蒽素嘧啶、黄烷士酮、皮蒽酮、蒽垛蒽酮、二噁嗪、三芳基碳鎓、喹酞酮颜料、二酮吡咯并吡咯红（“DPPBO 红”）、二氧化钛、炭黑和它们的混合物。术语“颜料”和“着色的填料”可以互换地使用。

[0061] 染料的例子包括但不限于，是溶剂和／或基于水的那些例如酸性染料、偶氮型染料、碱性染料、直接染料、分散染料、活性染料、溶剂染料、硫化染料、媒染染料，例如，钒酸铋、蒽醌、二萘嵌苯、铝、喹吖啶酮、噻唑、噻嗪、偶氮、靛蓝、硝基、亚硝基、噁嗪、酞菁、喹啉、芪、和三苯基甲烷。

[0062] 染料剂的例子包括，但不限于，分散于基于水的或水可混溶的载体的颜料，例如商购自Degussa, Inc. 的AQUA-CHEM 896，商购自Eastman Chemical, Inc的Accurate Dispersion分部的CHARISMA着色剂和MAXITONER INDUSTRIAL着色剂

[0063] 如上所述，着色剂可以是分散体的形式，所述形式包括，但不限于，纳米颗粒分散体。纳米颗粒分散体可包括产生期望的目视颜色和／或不透明性和／或目视效果的一种或多种高度分散的纳米颗粒着色剂和／或着色剂颗粒。纳米颗粒分散体可包括着色剂，例如具有小于150nm，例如小于70nm，或小于30nm的粒度的颜料或染料。纳米颗粒可通过用具有小于0.5mm的粒度的研磨介质研磨原料有机或无机颜料来制备。纳米颗粒分散体的例子和制备它们的方法描述于美国专利号6,875,800B2中，其通过引用并入本文。纳米颗粒分散体还可通过结晶、沉淀、气相冷凝、和化学磨损（即，部分溶解）来制备。为了最小化涂料内纳米颗粒的再团聚，可以使用树脂涂覆的纳米颗粒的分散体。本文使用的“树脂涂覆的纳米颗粒的分散体”是指在其中分散了离散的“复合微粒”的连续相，所述复合微粒包含纳米颗粒和在纳米颗粒上的树脂涂料。树脂涂覆的纳米颗粒分散体的例子和制备它们的方法描述于2004年6月24日提交的美国申请号10/876,031，其通过引用并入本文，和2003年6月24日提交的美国临时申请号60/482,167中，其也通过引用并入本文。

[0064] 可以用于本发明涂料中的特殊效果组合物的例子包括产生一种或多种外观效应例如反射率、珠光性、金属光泽、磷光性、荧光性、光致变色性、光敏性、热致变色性、随角异色(goniochromism)和／或颜色改变的颜料和／或组合物。另外的特殊效果组合物可提供其它可察觉的性质，例如反射性、不透明性或纹理。在非限制性的实施方式中，特殊效果组合物可产生色移，以使得当以不同角度观察涂层时，涂层颜色改变。颜色效果组合物的例子描述于美国专利号6,894,086中，其通过引用并入本文。另外的颜色效果组合物可包括透明涂覆的云母和／或合成的云母、经涂覆的二氧化硅、经涂覆的氧化铝、透明的液晶颜料、液晶涂料和／或其中干涉由材料内的折射指数差异引起而不是由于材料表面和空气之间的折射指数差异的任何组合物。

[0065] 在某些非限制性的实施方式中，当暴露于一种或多种光源时，可逆地改变其颜色的光敏组合物和／或光致变色组合物可用于本发明的涂料中。光致变色和／或光敏组合物可通过暴露于特定的波长来活化。当组合物受到激发时，分子结构改变并且该改变的结构显示出不同于组合物的原始颜色的新的颜色。当移除对辐射的暴露时，光致变色和／或光敏组合物可恢复到静态，其中恢复组合物的原始颜色。在一种非限制性的实施方式中，光致变色和／或光敏组合物在非激发态下是无色的并且在激发态显示出颜色。完全的颜色改变可在几毫秒至几分钟内，例如20秒-60秒内出现。光致变色和／或光敏组合物的例子包括光致变色染料。

[0066] 在非限制性的实施方式中，光敏组合物和／或光致变色组合物可与聚合物和／或可聚合组分的聚合物型材料关联和／或至少部分键连，例如通过共价键合。与其中光敏组合物可以迁移出涂料并且结晶到基材中的一些涂料相反，根据本发明的非限制性实施方式

与聚合物和／或可聚合的组分关联和／或至少部分键连的光敏组合物和／或光致变色组合物，具有最小的迁移出涂料的量。光敏组合物和／或光致变色组合物的例子和制备它们的方法描述于 2004 年 7 月 16 日提交的美国专利申请序列号 10/892,919 中，其通过引用并入本文。

[0067] 通常，着色剂可以以足以赋予期望的性质，目视和／或颜色效果的任意量存在于涂料组合物中。着色剂可占本发明组合物的 1-65 重量％，例如 3-40 重量％或 5-35 重量％，且重量％基于所述组合物的总重量计。

[0068] 本发明的能固化成膜组合物可含有常规地用于表面涂层的彩色颜料并且可用作无光光洁度或“低光泽度”单涂层；即，低光泽度着色涂料。“低光泽度”是指固化涂层具有小于 30，经常小于 20 的初始 85° 光泽度测量值，其由本领域技术人员已知的标准技术测量。这种标准技术包括用于光泽测量的 ASTM D523。

[0069] 本发明的能固化成膜组合物可备选地用作多层复合涂料组合物的无光光洁度清漆层，例如彩色－加－澄清的复合涂料，如下所述。

[0070] 本发明的能固化成膜组合物可在环境温度或升高的温度下能固化（取决于采用的交联化学过程）。本发明的成膜组合物最适用作面漆，特别是，清漆和单涂层，凭借如下所述的它们的无光光洁度和耐抛光性性质。该组合物可通过成分的简单混合，使用本领域周知的配制技术简单地制备。

[0071] 本发明的组合物可施涂于任意各种基材（例如金属、玻璃、木材，和／或聚合物型基材），并且可以用常规的方式（包括但不限于刷涂、浸涂、浇涂、喷涂等）来施涂。它们最经常通过喷涂来施涂。可以使用的用于空气喷涂、真空喷涂，和静电喷涂的通常的喷涂技术和设备，其采用手动和／或自动方法。合适的基材包括但不限于金属基材例如黑色金属、锌、铜、镁、铝、铝合金、以及典型地用于汽车和其它车身的制造中的其它金属和合金基材。黑色金属基材可包括铁、钢、及其合金。有用的钢材的非限制性的例子包括冷轧钢、镀锌的（锌涂覆的）钢、电镀锌的钢、不锈钢、酸洗钢，锌－铁合金例如 GALVANNEAL，及其组合。还可以使用黑色金属和有色金属的组合或复合材料。

[0072] 本发明的组合物还可施涂于弹性体、塑料或复合材料基材例如在机动车上发现的那些。“塑料”是指任何常见的热塑性或热固性合成非导电性材料，包括热塑性烯烃例如聚乙烯和聚丙烯、热塑性聚氨酯、聚碳酸酯、热固性片状成型化合物、反应注射成型化合物、基于丙烯腈的材料、尼龙等。“复合材料”是指由纤维组成的任何基材（典型地由玻璃或碳组成），或与聚合物型或塑性材料一起引入的其它填料材料，常见的是环氧类型的聚合物。

[0073] 通过任何常规的涂覆技术（包括但不限于任何以上公开的那些）可将本发明的能固化成膜组合物施涂于基材或底漆之上。透明的面漆可施涂于固化的底漆或在底漆固化之前的干燥的底漆。在后者的情况下，两种涂料可然后被加热以同时固化涂覆层。

[0074] 在底漆不是由本发明组合物形成的情况下（但是面漆是由本发明的能固化涂料组合物形成的），在彩色－加－澄清系统中的底漆涂料组合物可以是任何可用于涂料应用（特别是汽车应用）的组合物。底漆的涂料组合物可包含树脂粘合剂和颜料和／或其它着色剂，以及在涂料组合物领域中周知的任选的添加剂。树脂粘合剂的非限制性的例子是丙烯酸类聚合物、聚酯、醇酸、和聚氨酯。

[0075] 可通过任何常规的涂覆技术（例如上述的那些）将底漆组合物施涂于上述的任何

基材，但是最经常通过喷涂来施涂。可以使用用于空气喷涂、真空喷涂、和静电喷涂的通常的喷涂技术和设备，其采用手动和／或自动方法。如果期望的话，得到的膜厚度可变化。

[0076] 在基材上形成底漆的膜之后，该底漆可固化或备选地被给予干燥步骤，其中在施涂清漆之前通过加热或空气干燥时间段将至少一些溶剂从底漆膜中除去。合适的干燥条件可取决于，例如，特定的底漆组合物，以及如果组合物是水性的，取决于环境湿度。

[0077] 可通过任何常规的涂覆技术（包括但不限于以上公开的那些）将透明或澄清的面漆组合物施涂于底漆。透明的面漆可施涂于固化的底漆或在底漆固化之前的干燥底漆。在后者的情况下，两种涂料可然后被加热以同时固化涂覆层。

[0078] 第二面漆涂料组合物可施涂于第一面漆以形成“清漆碰清漆 (clear-on-clear)”的面漆。第一面漆涂料组合物可施涂于如上所述的底漆。第二面漆涂料组合物可施涂于固化的面漆或在底漆和第一面漆固化之前的干燥的第一面漆。底漆，第一面漆和第二面漆可然后被加热以同时固化三种涂覆层。

[0079] 应理解第二透明的面漆和第一透明的面漆涂料组合物可以相同或不同，条件是，当以湿碰湿工艺施涂时，一面漆没有显著地干扰另一面漆的固化，例如，通过抑制溶剂／水从较低的层蒸发。此外，第一面漆和第二面漆均可以是本发明的能固化涂料组合物。备选地，只有第二面漆可由本发明的能固化涂料组合物形成。

[0080] 如果第一面漆不包含本发明的能固化涂料组合物，其可，例如，包括含能热固性涂料材料和固化剂的任何能交联的涂料组合物。

[0081] 典型地，在底漆上形成第一面漆之后，第一面漆被给予干燥步骤，其中通过在施涂第二面漆之前加热或，备选地，空气干燥时间段或固化步骤将至少一些溶剂从膜中除去。合适的干燥条件取决于所使用的特定成膜组合物。

[0082] 当作为第二面漆涂料组合物使用时，本发明的成膜组合物可与上所述的第一面漆一样，通过任何常规的涂料施涂技术来施涂。固化条件可以是上述用于面漆的那些。

[0083] 本发明的能固化成膜组合物，在作为涂料施涂于基材之后并且在固化之后，当经受湿磨测试方法一时，显示出小于 30，例如小于 20 或小于 10 的初始 85° 光泽度，以及不大于 10 光泽度单位，或不大于 5 光泽度单位的 85° 光泽度的增加。在本发明的某些实施方式中，在经受磨损测试后，能固化成膜组合物甚至会显示出光泽的降低。

[0084] 另外地，在本发明的某些实施方式中，本发明的能固化成膜组合物，在作为涂料施涂于基材之后并且在固化之后，当经受湿磨测试方法二时，显示出小于 30，例如小于 20 或小于 10 的初始 85° 光泽度，以及不大于 15 光泽度单位，或不大于 10 光泽度单位的 85° 光泽度的增加。在本发明的某些实施方式中，在经受磨损测试后，能固化成膜组合物甚至会显示出光泽的降低。

[0085] 湿磨测试方法一和二中的每一个分别对应于以 10 或 40 个循环运行的 Amtec-Kistler Car Wash Test DIN 55668。在湿磨测试一和二中，通过首先测量涂层的（“原始光泽度”）85° 光泽度，使基材上固化的涂层经受测试。然后，使涂层经受以 10 或 40 次循环运行的 Amtec-Kistler Car Wash Test DIN 55668，并且之后，再次测量 85° 光泽度。

[0086] 本发明的能固化成膜组合物，在作为涂料施涂于基材之后并且在固化之后，当经受干磨测试方法一时，显示出小于 30，例如小于 20 或小于 10 的初始 85° 光泽度，以及不大

于15光泽度单位，或不大于10光泽度单位的85° 光泽度的增加。另外地，在本发明的某些实施方式中，本发明的能固化成膜组合物，在作为涂料施涂于基材之后并且在固化之后，当经受干磨测试方法二时，显示出小于30，例如小于20或小于10的初始85° 光泽度，以及不大于15光泽度单位，或不大于10光泽度单位的85° 光泽度的增加。

[0087] 进行干磨测试方法一和二中的每一个以使得涂层被线性刮擦，其使用Atlas AATCC CROCKMETER，Model CM-5（得自Chicago，Ill的Atlas Electric Devices Company）用加重的砂纸来回摩擦十次。所用的砂纸是3M 281Q WETORDRY™ PRODUCTION™2和9微米抛光纸片（其商购自St. Paul，Minn的3M Company），分别用于干磨测试方法一和二。在干磨测试一和二中，通过首先测量涂层的（“原始光泽”）85° 光泽度使基材上的固化的涂层经受测试。然后使该涂层经受干磨测试一和二，以及之后，再次测量85° 光泽度。

[0088] 考虑到它们的独特性质，本发明的能固化成膜组合物特别适用于改进根据本发明的基材的耐抛光性的方法。该方法包括：(1) 将能固化成膜组合物施涂于基材以形成经涂覆的基材，以及 (2)(a) 将经涂覆的基材加热到足以固化能固化成膜组合物的温度和时间或 (b) 给予足以在环境条件下固化能固化成膜组合物的时间。能固化成膜组合物包含任意上述的那些并且形成在经涂覆的基材上的最外层，或面漆。

[0089] 在以下实施例中更详细地描述本发明，所述实施例旨在仅仅是示例性的，这是由于其中的许多改变和变体对于本领域技术人员来说是明显的。除非另有说明，所有的份数和百分比是以重量计的。

[0090] 实施例A

[0091] 该实施例描述了氨基硅烷处理的二氧化硅消光剂的制备。

[0092] Hi-Si l 2000P(PPG Industries的沉淀二氧化硅产品 (BET表面积为225m^2/g)）被研磨并且分类成10微米的体积平均粒度（通过BeckmanCoulter LS 230仪器测量）及22.5微米的最大粒度。该二氧化硅用16%氨基丙基三乙氧基硅烷（Dow Corning的Z-6011，也称为3-三乙氧基甲硅烷基丙胺以及其化学式是$H_2N(CH_2)_3Si(OC_2H_5)_3$）处理，该处理是通过将其在Waring共混机中共混，且连续地用配有氟橡胶油管的Masterflex泵以均匀的速率使硅烷泵出（持续五分钟）。使均匀的共混物在对流烘箱中在120摄氏度下经受两小时。在胺硅烷反应之后，二氧化硅样品具有2.3%碳，2.1%水分，267ml邻苯二甲酸二丁酯/100g吸油量，189m^2/gBET表面积，10.2微米体积中等粒度。

[0093] 实施例1和2显示了根据本发明的能固化成膜组合物的制备。通过首先混合成分的分离的组分，以及然后在施涂于基材之前立即将组分结合来制备该组合物。

[0094]

成分	实施例 1： 重量(g)	实施例 2： 重量(g)
A-组分：		
D8150[1]	42.1	42.1
胺官能二氧化硅[2]	5.06	7.16
D871[1]	18.5	20.0
B-组分：		
D8371[1]	15.4	15.4

[0095] [1]得自 PPG Industries，Inc.

[0096] [2]如以上实施例 A 所述

[0097] 将实施例 1 和 2 的成膜组合物喷涂至着色的底漆以在电涂有底漆的钢板上形成彩色-加-澄清的复合涂层。所用的板是带有 ED6060 电涂（得自 ACT Laboratories，Inc）的 ACT 冷轧钢板（10.16cm 乘以 30.48cm）。用 ENVIROBASE 高性能（EHP）着色的水性底漆（得自 PPGIndustries，Inc）涂覆分离的板。使用带有 WSB 流体喷嘴的 SATAjet3000 在环境温度（约 70° F(21℃)）下手工喷涂 Black EHP T407。底漆的目标干膜厚度是约 0.3-0.8 密尔（约 7-20 微米）。在施涂清漆之前，使底漆板在环境温度（约 70° F(21℃)）下闪蒸至少 15 分钟。

[0098] 在环境温度下，使用 Devilbiss GTi HVLP 喷枪将每种涂料组合物手工喷以两涂层涂至涂有底漆的板，且在施涂之间进行环境闪蒸。清漆的目标干膜厚度为 1.5-2.5 密尔（约 38-64 微米）。使所有的涂料在环境温度下固化或空气闪蒸约 20 分钟，之后被烘焙。任选的烘焙是在 140° F(60℃)下进行三十分钟。在施涂清漆七天之后，使经涂覆的板经受干磨测试方法一和二以及湿磨测试方法一和二以测定耐抛光性。下表 1 显示了湿磨测试方法的结果以及表 2 显示了实施例 1 的能固化成膜组合物的干磨测试方法的结果。

[0099] 表 1

[0100]

涂层	原始 85°光泽度	在湿磨测试方法一之后的光泽度	在湿磨测试方法二之后的光泽度
实施例 1	13.4	17.8	27
实施例 2	5.3	6.7	9.2

[0101] 表 2

[0102]

涂层	原始 85°光泽度	在干磨测试方法一之后的光泽度	在干磨测试方法二之后的光泽度
实施例 1	13.4	23.9	25.6
实施例 2	5.3	11.0	13.6

[0103] 表中的数据表明本发明的能固化成膜组合物显示出优良的耐抛光性。对于湿磨测试方法一，实施例涂层显示出小于 5 光泽度单位的光泽增长。同样地，对于干磨测试方法二，实施例涂层显示出 12.2 或更少的光泽度单位的光泽增长。

[0104] 已经参照本发明特定实施方式的具体细节描述了本发明。除了它们包括在所附权利要求中的范围和程度之外，并不旨在认为这样的细节是对本发明范围的限制。