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(54) **Title:** REACTIVE DILUENTS FOR MODIFYING THERMOSETTING PAINT COMPOSITIONS AND PAINT COMPOSITIONS IN WHICH THEY ARE USED.

(57) **Abstract:** To provide paint compositions with which paint films which have excellent acid resistance, water resistance and weather resistance, and in particular excellent car-wash scratching resistance, can be formed and reactive diluents which can be used for obtaining these paint compositions. [Means of Resolution] A reactive diluent comprising a hydroxyl group containing resin which has been obtained by reacting (a) a compound where two or more hydroxyl groups are included in one molecule, (b) a compound where two non- sulfur modified isocyanate groups are included in one molecule and (c) a lactone compound, characterized in that said hydroxyl group containing resin has a hydroxyl group value of from 100 to 200 mgKOH/g and a weight average molecular weight of from 1,000 to 2,000, and contains from 20 to 40 mass% of structural units based on the lactone compound of the (c) component, and thermosetting paint compositions which contain these reactive diluents and hydroxyl group containing acrylic resins.

Reactive diluents for modifying thermosetting paint compositions and paint compositions in which they are used.

[Technical Field]

[0001]

The invention concerns novel reactive diluents and paint compositions in which these reactive diluents are used for obtaining paint films which have excellent acid resistance and weather resistance and, in particular, excellent car-wash scratching resistance, in the automobile paint field for example.

[Technical Background]

[0002]

Paint compositions which are characterized in that they contain from 10 to 50 wt% urethane polyol of weight average molecular weight from 1500 to 4000 and hydroxyl group value from 50 to 180 mgKOH/g which have been obtained by reacting isocyanate compound and caprolactone polyol, from 30 to 80 wt% of fluorinated resin copolymer of hydroxyl group value from 50 to 150 mgKOH/g in which fluoro-olefin has been reacted as essential raw material and from 10 to 40 wt% of crosslinking agent are known as a method of rendering a paint film for automobile purpose unlikely to scratch in a car-wash (for example, see Patent Citation 1). However, with these paint compositions the car-wash

scratching resistance is inadequate and so the initial state is not maintained because of scratches which are produced when car-washing and, furthermore, there is a problem in that they are expensive since they contain fluorine.

[0003]

Furthermore, paint compositions which are characterized in that they contain polyester oligomers of which the primary hydroxyl group content is from 3 to 5 groups per molecule and the number average molecular weight is from 1501 to 3000 which are from 30 to 85% lactone modified and which have aliphatic hydrocarbyl groups which have from 4 to 22 carbon atoms originating from the lactone, and amino resin-based hardening agents which react with the hydroxyl groups of the aforementioned hydroxyl group containing polyester oligomers, are known as paint compositions which have excellent gasoline resistance, scratching resistance, acid resistance and water resistance and which have in particular excellent chipping resistance (for example, see Patent Citation 2). However, with these paint compositions there is a problem in that the acid rain resistance is reduced because an amino resin forms an essential component.

[0004]

Furthermore, compositions comprising (A) hydroxyl group containing solvent soluble fluorine containing

copolymer which has fluoro-olefin based polymer units and vinyl-based polymer units which have suspended polyester chains, (B) polycaprolactone polyol which has a number average molecular weight of from 200 to 3000, which has terminal hydroxyl groups and which has a hydroxyl group value of from 40 to 800 mgKOH/g and (C) hardening agent which has functional groups which react with hydroxyl groups are known as paint compositions which have excellent durability (scratching resistance) in respect of scratches caused by wiping with a duster or an automatic car-washing machine and chips caused by flying gravel and the like which is thrown up when driving (for example, see Patent Citation 3). However, with these paint compositions the car-wash scratching resistance is inadequate and so the initial state is not maintained due to scratches which are produced when car-washing and, furthermore, there is a problem in that they are expensive since they contain fluorine.

[0005]

Furthermore, paint compositions which have as essential components hydroxyl group containing resins (A) which have a hydroxyl group value of from 200 to 400 mgKOH/g, and which include not more than 25 mass% of structural units based on lactone compounds in the resin solid fraction, hydroxyl group containing resins (B) which have a hydroxyl group value of from 50 to 200 mgKOH/g and which include from 25 to 75 mass% of

units based on lactone compounds in the resin solid fraction, crosslinking agent (C) which includes at least one or more functional group which reacts with hydroxyl groups in the molecules which are characterized in that the proportions of the hydroxyl group containing resin (A) and the hydroxyl group containing resin (B), as the mass ratio of the resin solid fractions, are (A)/(B) from 90/10 to 10/90 are known as paint compositions with which paint films which have excellent car-wash scratching resistance, acid resistance, staining resistance, water resistance and weather resistance can be obtained (for example, see Patent Citation 4). However, these hydroxyl group containing resins (A) and (B) are both acrylic resins which have a weight average molecular weight of from 1,000 to 30,000 and the flexibility is inadequate and so there is a problem in that the car-wash scratching resistance is inadequate.

[0006]

[Patent Citation 1]

Japanese Unexamined Patent Application Laid Open H5-051556

[Patent Citation 2]

Japanese Unexamined Patent Application Laid Open H8-217876

[Patent Citation 3]

Japanese Patent 3029627

[Patent Citation 4]

Japanese Unexamined Patent Application Laid Open 2007-039574

[Disclosure of the Invention]

[Problems to be Resolved by the Invention]

[0007]

To provide paint compositions with which a paint film which has excellent acid resistance, staining resistance, water resistance and weather resistance and which has in particular excellent car-wash scratching resistance in the paint field for automobile purposes, and a reactive diluent which can be used for obtaining this paint composition.

[Means of Resolving These Problems]

[0008]

As a result of thorough research carried out with a view to resolving the abovementioned problems the inventors have discovered that the abovementioned problems can be resolved by compounding a reactive diluent comprising a hydroxyl group containing resin which has been obtained by reacting (a) compound which includes two or more hydroxyl groups in one molecule, (b) compound which includes two non-sulfur modified isocyanate groups in one molecule and (c) lactone compound where said hydroxyl group containing resin has a specified hydroxyl group value, a specified weight average molecular weight and a specified content of

structural units based on the lactone compound of component (c) in a paint composition, and that a paint films which has in particular excellent car-wash scratching resistance can be formed, and the present invention is based upon this discovery.

[0009]

That is to say, the invention provides a reactive diluent comprising a hydroxyl group containing resin which has been obtained by reacting at the same time (a) a compound where two or more hydroxyl groups are included in one molecule, (b) a compound where two non-sulfur modified isocyanate groups are included in one molecule and (c) a lactone compound which is characterized in that said hydroxyl group containing resin has a hydroxyl group value of from 100 to 200 mgKOH/g and a weight average molecular weight of from 1,000 to 2,000, and contains from 20 to 40 mass% of structural units based on the lactone compound of the (c) component.

[0010]

Furthermore, the invention provides a reactive diluent comprising a hydroxyl group containing resin which has been obtained by reacting (a) a compound where two or more hydroxyl groups are included in one molecule and (b) a compound where two non-sulfur modified isocyanate groups are included in one molecule and then carrying out an addition reaction of (c) a

lactone compound, characterized in that said hydroxyl group containing resin has a hydroxyl group value of from 100 to 200 mgKOH/g and a weight average molecular weight of from 1,000 to 2,000, and contains from 20 to 40 mass% of structural units based on the lactone compound of the (c) component.

[0011]

Furthermore, the invention provides a thermosetting paint composition, characterized in that it includes the abovementioned reactive diluent, hydroxyl group containing acrylic resin which has a hydroxyl group value of from 80 to 150 mgKOH/g and a weight average molecular weight of from 3,000 to 100,000 and polyfunctional isocyanate compound and in which the proportion of the contents of said reactive diluent and said hydroxyl group containing acrylic resin as the resin mass ratio is within the range from 5/95 to 15/85.

Furthermore, the invention provides a thermosetting paint composition in which, in the abovementioned thermo-setting paint composition, the polyfunctional isocyanate compound is an isocyanurate compound.

[Effect of the Invention]

[0012]

On using a reactive diluent of this invention in a thermosetting paint composition it functions as a

diluent and reacts with the hardening agent and forms a hardened resin component, and paint films which have excellent acid resistance and weather resistance can be formed, and in particular paint films which have excellent car-wash scratching resistance can be formed and, furthermore, the painting operability is excellent. Furthermore, the compatibility with the hydroxyl group containing resins which are used as the resin components of thermo-setting paint compositions is excellent.

[Embodiment of the Invention]

[0013]

A reactive diluent of this invention is obtained by reacting (a) compound which includes two or more hydroxyl groups, (b) compound which includes two non-sulfur modified isocyanate groups and (c) lactone compound, and the (a) component, the (b) component and the (c) component may be reacted at the same time or the (a) component and the (b) component may be reacted first and then an addition reaction can be carried out with the (c) component.

The (a) component which is used in the invention is a compound where two or more hydroxyl groups are included in one molecule, and the polyhydric alcohols which are generally used as polyester raw materials can be cited as ideal practical examples. However, radically polymerizable monomers and acrylic resin

oligomers which have been obtained by polymerizing radically polymerizable monomers are undesirable for the (a) component of this invention in that flexibility is difficult to achieve.

[0014]

Examples of actual polyhydric alcohols of the (a) component include the following dihydric and trihydric and higher alcohols. Examples of the dihydric alcohols include glycols such as ethylene glycol propylene glycol, diethylene glycol, triethylene glycol, 1,4-butanediol, 1,3-butanediol, 2,3-butanediol, 1,2-butanediol, 1,5-pentanediol, 1,4-pentanediol, 2,4-pentanediol, 2,3-dimethyltrimethylene glycol, tetramethylene glycol, 3-methyl-4,5-pentanediol, 2,2,4-trimethyl-1,3-pentanediol, 1,6-hexanediol, 1,5-hexanediol, 1,4-hexanediol, 2,5-hexanediol, 1,4-cyclohexanedimethanol, neopentyl glycol and the like, polyether polyols such as alkylene oxide adducts of bisphenol A, polyethylene glycol, polypropylene glycol and the like, mono-epoxy compounds such as α-olefin epoxides such as propylene epoxide and butylene epoxide and the like and Cardura E-10 (trade name, a glycidyl ester of synthetic highly branched saturated fatty acid, produced by the Shell Chemical Co.) and the like, dihydric polyols which include acid groups such as dimethylolpropionic acid, dimethylol-butanoic acid and the like, and alicyclic polyols such

as 1,4-cyclohexanediol, hydrogenated bisphenol A, cyclohexyldimethylol and the like.

[0015]

Furthermore, glycerine, trimethylolethane, trimethylolpropane, diglycerine, pentaerythritol, dipentaerythritol, sorbitol and the like can be cited as examples of trihydric and higher alcohols and, furthermore, compounds which have two or more epoxy groups in the molecule such as bisphenol A diglycidyl ether can also be used as trihydric or higher alcohols.

From among the abovementioned polyhydric alcohols trimethylolpropane, dimethylolpropionic acid, dimethylolbutanoic acid, hydrogenated bisphenol A and 1,4-cyclohexanedimethanol are preferred from the viewpoint of the balance between the flexibility and hardness of the paint compositions in which the reactive diluent is used, and combinations of trimethylolpropane (TMP) and 1,4-cyclohexanedimethanol (CHDM) in which the TMP and CHDM mol ratio is within the range from 15/85 to 45/55 are more desirable, and those combinations where the mol ratio is within the range from 20/80 to 40/60 are especially desirable, from the viewpoint of the balance of hardness and flexibility.

[0016]

Furthermore, the dimethylolalkanoic acids such as dimethylolpropionic acid and dimethylolbutanoic acid

which have carboxyl groups among the polyhydric alcohols fortunately also fulfill the role as acid catalysts for esterification reactions and urethanization reactions, but an acid catalyst may be used in those cases where a dimethylolalkanoic acid is not used.

One type of polyhydric alcohol may be used alone, or a combination of two or more types can be used.

Furthermore, low molecular weight polyesters where polyols which have two or more hydroxyl groups and carboxylic acids which have two or more carboxyl groups have been pre-reacted beforehand may be used for the (a) component which is used in the invention, but the polyesters which have a linear structure obtained from polyols which have two hydroxyl groups and carboxylic acids which have two carboxyl groups are preferred from the flexibility viewpoint.

[0017]

The (b) component used in the invention is a compound which includes two non-sulfur modified isocyanate groups in one molecule.

Aliphatic di-functional isocyanates such as hexamethylene diisocyanate (HDI) and alicyclic difunctional diisocyanates such as isophorone diisocyanate (IPDI), 4,4'-diphenylmethanediisocyanate (MDI) and 4,4'methylenebis(cyclohexylisocyanate) (hydrogenated MDI) can be used as actual examples of

the (b) component, but isophorone diisocyanate is especially desirable from the viewpoint of the balance of flexibility and hardness of a paint composition in which the reactive diluent is used.

One type of (b) component may be used alone, or a combination of two or more types can be used.

[0018]

ε-Caprolactone, γ-butyrolactone, δ-valerolactone, γ-valerolactone, γ-caprolactone, γ-nonanoiclactone, δ-dodecanolactone and the like can be cited as actual examples of the lactone compounds which can be used for the (c) component of this invention, but ε-caprolactone in particular is preferred. One type of lactone may be used for the (c) component, or a combination of two or more types may be used.

The hydroxyl group value of a hydroxyl group containing resin which is a reactive diluent of this invention is preferably from 100 to 200 mgKOH/g, more desirably from 130 to 190 mgKOH/g, and most desirable from 150 to 190 mgKOH/g. With a hydroxyl group value of the hydroxyl group containing resin which is a reactive diluent of less than 100 mgKOH/g paint film hardness is not obtained and the staining resistance is reduced, and in those cases where it exceeds 200 mgKOH/g the SP (solubility parameter) value of the resin rises and differs from the SP value of the hardening agent and the compatibility is reduced and so

appearance-failure of the paint film occurs.

[0019]

The weight average molecular weight of a hydroxyl group containing resin which is a reactive diluent of this invention is preferably from 1,000 to 2,000, more desirably from 1,400 to 2,000, and most desirably from 1,600 to 1,800. With a weight average molecular weight of the hydroxyl group containing resin which is a reactive diluent of this invention of less than 1,000 it is difficult to obtain satisfactory film hardness, and in those cases where it exceeds 2,000 appearance-failure of the paint film arises due to the reduced compatibility with hydroxyl group containing acrylic resins.

The proportion of the (c) component included in a hydroxyl group containing resin which is a reactive diluent of this invention as structural units based on a lactone compound in the hydroxyl group containing resin which is a reactive diluent is preferably from 20 to 40 mass%, more desirably from 25 to 40 mass%, and most desirably from 30 to 40 mass%. With a proportion of (c) component of the hydroxyl group containing resin which is a reactive diluent of less than 20 mass% the car-wash scratching resistance of the paint film is reduced, and in those cases where it exceeds 40 mass% the compatibility of the paint is reduced and the hardness and staining resistance of the paint film are

reduced.

[0020]

The reaction for obtaining a hydroxyl group containing resin which is a reactive diluent comprises two reactions, namely an addition reaction I of a compound which includes two or more hydroxyl groups which is the (a) component and a compound which includes two non-sulfur modified isocyanate groups which is the (b) component, and the addition reaction II of a lactone compound which is the (c) component on the hydroxyl groups of the compound which includes two or more hydroxyl groups which is the (a) component or the compound obtained in addition process I.

The addition reaction I involves reaction for from 1 to 3 hours under temperature conditions from 110 to 130°C and addition reaction II involves reaction for from 2 to 4 hours under temperature conditions from 140 to 160°C.

Both in those cases where the (a) component, the (b) component and the (c) component are all introduced into a reaction vessel and reacted at the same time, and in those cases where the (a) component and the (b) component are pre-reacted and then reacted with the (c) component, a reaction process with reaction initially under the conditions of addition reaction I and then reaction under the conditions of addition reaction II is preferred from the viewpoints of reaction efficiency

and safety.

[0021]

A reaction catalyst which can be used in urethane paints generally can be used in the reaction of the isocyanate compound and the hydroxyl group containing compound in addition reaction I.

The tin-based catalysts such as dibutyltin dilaurylate, acid-based catalysts such as organic carboxylic acids and basic catalysts such as tertiary amines can be cited as actual reaction catalysts.

Furthermore, the reactive diluent can be synthesized in a solvent, but preferably alcohol-based solvents are not used so that there is no reaction with the isocyanate groups. Aromatic solvents, ester-based solvents, ketone-based solvents and the like can be cited as preferred solvents.

The reactive diluent may include solvent but a smaller the solvent content is desirable. The preferred solvent content is preferably not more than 50 mass%, and more desirably not more than 45 mass%, with respect to the total amount of reactive diluent.

[0022]

A reactive diluent of this invention can be used for a thermosetting paint composition in which it is used with a poly-functional isocyanate compound which is a crosslinking agent which reacts with the hydroxyl groups of the hydroxyl group containing resin which is

the reactive diluent and the hydroxyl groups of a hydroxyl group containing acrylic resin.

A reactive diluent of this invention fulfils the role of the modifying agent of a hydroxyl group containing acrylic resin and the mixing proportions of reactive diluent and hydroxyl group containing acrylic resin as the resin mass ratio is preferably in the range from 5/95 to 15/85, and more desirably in the range from 7/93 to 13/87.

With a mixing proportion of reactive diluent of less than 5 mass% the paint film hardness is inadequate, and in those cases where it exceeds 15 mass% the weather resistance is reduced as a result of the effect of the reactive diluent which includes much low molecular weight material.

[0023]

The hydroxyl group containing acrylic resin can be obtained by copolymerizing a hydroxyl group containing acrylic monomer with other radically polymerizable monomer in accordance with the usual acrylic resin synthesizing conditions.

Furthermore, the weight average molecular weight of the hydroxyl group containing acrylic resin is preferably from 3,000 to 100,000, more desirably from 3,000 to 50,000, and most desirably from 4,000 to 30,000. With a hydroxyl group containing acrylic resin of weight average molecular weight less than 3,000 the

hardenability is poor, and in those cases where it exceeds 100,000 the viscosity when forming a paint film is high and so the paint film appearance declines.

Furthermore, the hydroxyl group value of the hydroxyl group containing acrylic resin is preferably from 80 to 150 mgKOH/g, and more desirably from 90 to 145 mgKOH/g.

[0024]

2-Hydroxyethyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, allyl alcohol, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, and the ethylene oxide and/or propylene oxide adducts of 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate and the like can be cited as hydroxyl group containing acrylic resin hydroxyl group containing monomers, but from the viewpoints of hardness and flexibility 4-hydroxybutyl (meth)acrylate is especially desirable.

[0025]

Actual examples of other radically polymerizable monomers which can be used in the hydroxyl group containing acrylic resin include methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, sec-butyl acrylate, hexyl acrylate, cyclohexyl acrylate, 2-ethylhexyl acrylate, octyl acrylate, lauryl acrylate, stearyl

acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, sec-butyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, 2-ethylhexyl methacrylate, octyl methacrylate, lauryl methacrylate, stearyl methacrylate, styrene, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide and the like, and one type, or a mixture of two or more types, can be used.

[0026]

A radical polymerization initiator may be compounded when carrying out the radical copolymerization of the abovementioned radically polymerizable monomers. Examples of radical polymerization initiators include azo compounds such as 2,2'-azobisisobutyronitrile, 2,2'-azobis-2,4-dimethylvaleronitrile, 4,4'-azobis-4-cyanovaleric acid, 1-azobis-1-cyclohexanecarbonitrile, dimethyl-2,2'-azobisisobutyrate and the like, and organic peroxides such as methyl ethyl ketone peroxide, cyclohexanone peroxide, 3,5,5-trimethylhexanone peroxide, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-bis(t-butylperoxy)cyclohexane, 2,2-bis(t-butylperoxy)octane, t-butylhydroperoxide, diisopropylbenzenehydroperoxide, dicumyl peroxide, t-butylcumyl peroxide, isobutyl peroxide, lauroyl peroxide, benzoyl peroxide,

diisopropylperoxydicarbonate, t-butylperoxy 2-ethylhexanoate, t-butylperoxy neodecanate, t-butylperoxy laurate, t-butylperoxy benzoate, t-butylperoxy isopropylcarbonate (sic) and the like. One of these radical polymerization initiators may be used alone, or a combination of two or more types can be used.

[0027]

No particular limitation is imposed upon the amount of radical polymerization initiator compounded, but an amount of from 0.01 to 20 mass% with respect to the total amount of radically polymerizable monomer is preferred. Reducing agents such as dimethylaniline, ferrous salts such as ferrous sulfate, ferrous chloride, ferrous acetate and the like, acidic sodium sulfite, sodium thiosulfate, rongalite and the like may, of course, be included, as required, in these radical polymerization initiator systems, but they must be selected with care so that the polymerization temperature is as low as possible.

Poly-functional isocyanate compounds are preferred for the hardening agents which are used in the abovementioned thermosetting paint compositions, and p-phenylene diisocyanate, biphenyl diisocyanate, tolylene diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate, 1,4-tetramethylene diisocyanate, hexamethylene diisocyanate, 2,2,4-trimethylhexane-1,6-diisocyanate, methylenebis(phenylisocyanate), lysine

methyl ester diisocyanate, bis(isocyanatoethyl) fumarate, isophorone diisocyanate, methylcyclohexyl diisocyanate, 2-isocyanatoethyl-2,6-diisocyanato-hexanoate and the biuret forms (three isocyanate groups per molecule) and isocyanurate forms (three isocyanate groups per molecule) of these and the like can be cited as actual examples of the poly-functional isocyanate compounds, but the isocyanurate compounds are preferred from the viewpoints of weather resistance and heat resistance.

[0028]

The isocyanate compound may or may not be blocked, and isocyanate compounds where polyisocyanate compounds which have two or more isocyanate groups in one molecule, for example polyisocyanates such as hexamethylene diisocyanate, phenylene diisocyanate, xylylene diisocyanate, isophorone diisocyanate and the like, have been blocked with an active methylene based blocking agent such as methyl acetoacetate, dimethyl malonate and the like, or an oxime-based blocking agent can be cited as examples of isocyanate compounds which have blocked isocyanate groups.

The preferred proportions in which the hydroxyl group containing resin which is the reactive diluent used in this invention, the hydroxyl group containing acrylic resin and the polyfunctional isocyanate compound are included are such that the amount of

isocyanate group compounded with respect to the hydroxyl groups in the reactive diluent and hydroxyl group containing acrylic resin as the functional group ratio is preferably from 1/0.5 to 1/1.5, and more desirably from 1/0.8 to 1/1.2.

[0029]

The thermosetting paint compositions of this invention can be used as they are, or they can be used with the addition of organic solvents and various additives, for example one or more of ultraviolet absorber, photo-stabilizer, antioxidant, surfactant, surface controlling agent, hardening reaction catalyst, anti-static agent, perfume, de-watering agent and rheology controlling agents such as polyethylene wax, polyamide wax, fine internally crosslinked type resin particles and the like, as required.

The thermosetting paint compositions of this invention may be used as clear paints, or coloring agents such as dyes and pigments may be compounded and they may be used as colored paints.

[0030]

The thermosetting paint compositions of this invention are preferably used as top-coat paint compositions. The finish-painting method of a top-coat paint of this invention may be, for example, a two-coat one-bake finish-painting method where a colored base-coat is painted on a base material and in the un-

crosslinked state a thermosetting paint composition of this invention is applied as a top-coat paint, the overcoat finish-painting method where a colored based coat is painted on a base material and, in the un-hardened state, a top-coat paint is applied and they are baked at the same time, and then a paint composition of this invention is applied as an over-coat paint and baked, and the finish-painting method in which, in the aforementioned over-coat finish-painting method, a primer paint is applied in order to ensure adhesion of the base-coat and, in the un-crosslinked state, a thermosetting paint composition of this invention is applied as an over-coat paint.

[0031]

The aforementioned colored base coat paints, top-coat paints, over-coat paints and primer paints are adjusted to the prescribed viscosity, sometimes by heating or by adding organic solvents and reactive diluents, as required, and then painting is carried out using a painting machine as generally used such as a painting machine of the air sprayer, electrostatic air sprayer, roll coater, flow coater or dipping type, or using a brush or a bar coater, applicator or the like. From among these spray painting is preferred.

Furthermore, examples of the base materials on which thermosetting paint compositions of this invention are painted include both organic materials

and inorganic materials such as wood, glass, metal, cloth, plastics, foams, elastomers, paper, ceramics, concrete, plaster-board and the like. These base materials may be in an un-surface-treated state, or a paint film may have been formed on the surface beforehand.

Practical examples have been indicated so far, but the method of finish-painting with a thermosetting paint composition of this invention is not limited by the practical examples.

[0032]

No particular limitation is imposed upon the thickness of the paint films which are obtained by painting a thermosetting paint composition of this invention, but generally a film thickness after drying of from 10 to 150 μm is preferred, and a film thickness after drying of from 10 to 100μm is especially desirable.

Examples of coated objects which can be obtained with the method of coating of this invention include structural materials, wooden products, metal products, plastic products, rubber products, worked paper, ceramic products, glass products and the like. In more practical terms these include automobiles and automobile parts (for example bodies, bumpers, spoilers, mirrors, wheels, interior decorative parts and the like, which are made of a variety of

materials), metal sheets such as steel sheets, bicycles, bicycle parts, materials used on roads (for example guard rails, traffic signs, sound-deadening walls and the like), materials used in tunnels (for example side wall panels and the like), ships, railway rolling stock, aircraft, furniture, musical instruments, domestic electrical goods, building materials, containers, office accessories, sports accessories, toys and the like.

[Illustrative Examples]

[0033]

The invention is described in more practical terms below by means of examples and comparative examples. Moreover, where there is no indication to the contrary "parts" and "%" signify "parts by mass" and "mass%" respectively. Moreover, the resin solid fraction is the residue on heating measured with the method described in JIS K5601-1-2.

[0034]

<Production of Reactive Diluent D-1>

1,4-Cyclohexanedimethanol (14.6 parts), 5.8 parts of trimethylolpropane, 1.6 parts of dimethylolbutanoic acid, 17.9 parts of isophorone diisocyanate, 22.1 parts of ε-caprolactone and 22.7 parts methyl amyl ketone were introduced into a four-necked flask which had been furnished with a thermometer, a Dean and Stark (a fractionator for removing water etc. in the

condensation reaction when synthesizing polyester), a reflux condenser, a nitrogen delivery tube and a stirrer and reacted for 5 hours 150°C and, after checking that the isocyanate peak in the infrared absorption spectrum had disappeared, the reaction was terminated. Subsequently 15.3 parts of methyl amyl ketone were added, with stirring, and a solution of the reactive diluent D-1 of resin solid fraction 62.0 mass%, hydroxyl group value 175 mgKOH/g, lactone content (content of structural units based on a lactone compound) 35.6 mass% and weight average molecular weight 1,800 was obtained.

[0035]

<Production of Reactive Diluent D-2>

1,4-Cyclohexanedimethanol (12.2 parts), 7.6 parts of trimethylolpropane, 1.6 parts of dimethylolbutanoic acid, 17.4 parts of isophorone diisocyanate and 20.8 parts methyl amyl ketone were introduced into a four-necked flask which hade been furnished with a thermometer, a Dean and Stark, a reflux condenser, a nitrogen delivery tube and a stirrer and reacted for 2 hours 120°C and, after checking that the isocyanate peak in the infrared absorption spectrum had disappeared, 23.2 parts of ε-caprolactone were introduced and reacted for 3 hours at 150°C and the reaction was terminated. Subsequently 17.2 parts of methyl amyl ketone were added, with stirring, and a

solution of the reactive diluent D-2 of resin solid fraction 62.0 mass%, hydroxyl group value 184 mgKOH/g, lactone content (content of structural units based on a lactone compound) 37.5 mass% and weight average molecular weight 1,800 was obtained.

[0036]

<Production of Reactive Diluents D-3 to D-9>

The reactive diluents D-3 to D-9 were synthesized in the same way as reactive diluent D-1 except that the raw materials were changed as shown in Table 1 and Table 2.

[0037]

Table 1

Reactive Diluent	D-1	D-2	D-3	D-4	D-5
Isophorone diisocyanate	17.9	17.4	20.4	22.0	18.1
1,4-Cyclohexanedimethanol (CHDM)	14.6	12.2	17.1	22.6	19.8
Dimethylolbutanoic acid	1.6	1.6	1.6	1.6	1.6
Trimethylolpropane (TMP)	5.8	7.6	4.0		2.0
Methyl amyl ketone	22.7	20.8	26.1	30.8	26.3
ε-Caprolactone	22.1	23.2	18.9	15.8	20.4
Methyl amyl ketone	15.3	17.2	11.9	7.2	11.7
TOTAL	100.0	100.0	100.0	100.0	100.0
Hydroxyl group value of the hydroxyl group containing resin (mgKOH/g)	175	184	144	125	162
Resin solid fraction of the hydroxyl group containing resin (mass%)	62.0	62.0	62.0	62.0	62.0
Lactone content of the hydroxyl group containing resin (mass%)	35.6	37.5	30.5	25.5	33.0
CHDM/TMP mol ratio	70/30	60/40	80/20	100/0	90/10
Weight average molecular weight of the hydroxyl group containing resin	1800	1800	1400	1500	1600

[0038]

Table 2

Reactive Diluent	D-6	D-7	D-8	D-9
Isophorone diisocyanate	31.2	18.4	30.5	14.4
1,4-Cyclohexanedimethanol (CHDM)	22.7	17.1	14.7	
Dimethylolbutanoic acid	1.6	1.6	1.6	1.6
Trimethylolpropane (TMP)		4.0	5.8	16.4
Methyl amyl ketone	37.1	24.8	31.2	10.7
ε-Caprolactone	6.4	20.8	9.4	29.6
Methyl amyl ketone	0.9	13.2	6.8	27.3
TOTAL	100.0	100.0	100.0	100.0
Hydroxyl group value of the hydroxyl group containing resin (mgKOH/g)	51	165	75	235
Resin solid fraction of the hydroxyl group containing resin (mass%)	62.0	62.0	62.0	62.0
Lactone content of the hydroxyl group containing resin (mass%)	10.3	33.6	15.1	47.7
CHDM/TMP mol ratio	100/0	80/20	70/30	0/100
Weight average molecular weight of the hydroxyl group containing resin	1800	810	3200	1200

[0039]

<Production of Hydroxyl Group Containing Acrylic Resin A-1>

Methyl amyl ketone (32.4 parts) was introduced into a four-necked flask which had been furnished with a thermometer, a reflux condenser, a stirrer and a dropping funnel and heated to and maintained at 140°C, with stirring, under a current of nitrogen. Next a drip-feed component where radically polymerizable monomer comprising 9 parts of styrene, 21.6 parts of 4-hydroxybutyl acrylate, 15.2 parts of n-butyl acrylate, 13.8 parts of n-butyl methacrylate and 0.4 part of acrylic acid and 0.8 part of t-butylperoxy-2-ethylhexanoate as polymerization initiator had been mixed together uniformly was drip-fed from the dropping funnel at an even rate over a period of 2 hours at a temperature of 140°C. After the drip-feed had been completed the temperature was maintained at 140°C for 1 hour and then the reaction temperature was lowered to 115°C. Subsequently a polymerization initiator solution where 0.2 part of t-butylperoxy-2-ethylhexanoate as polymerization initiator had been dissolved in 6.6 parts of xylene was added as supplementary catalyst and the reaction was completed by maintaining the temperature at 115°C for a further period of 2 hours, and the hydroxyl group containing resin A-1 was obtained.

[0040]

<Production of Hydroxyl Group Containing Acrylic Resins A-2 to A-4>

Hydroxyl group containing resins A-2 to A-4 were obtained in the same way as the hydroxyl group containing resin A-1 except that the raw materials were changed as shown in Table 3.

[0041]

Table 3

		A-1	A-2	A-3	A-4
Reaction Solvent	Methyl amyl ketone	32.4	32.4	32.4	32.4
Drip-fed Monomer	Isobutyl methacrylate		10.2	12.0	3.0
	2-Ethylhexyl acrylate			13.2	21.0
	Styrene	9.0		6.0	3.0
	4-Hydroxybutyl acrylate	21.6			
	2-Hydroxyethyl acrylate		12.4	5.0	
	2-Hydroxyethyl methacrylate				19.4
	Butyl acrylate	15.2	37.0	23.4	13.2
	Butyl methacrylate	13.8			
	Acrylic acid	0.4	0.4	0.4	0.4
Initiator	Organic peroxide	0.8	0.5	0.8	5.0
Supplementary Catalyst	Organic Peroxide	0.2	0.2	0.2	0.2
	Xylene	6.6	6.9	6.6	2.4
TOTAL		100.0	100.0	100.0	100.0
Hydroxyl group value of the hydroxyl group containing acrylic resin (mgKOH/g)		140	100	40	140
Acid value of the hydroxyl group containing acrylic resin (mgKOH/g)		5	5	5	5
Resin solid fraction of the hydroxyl group containing acrylic resin (mass%)		61.0	60.7	61.0	65.2
Weight average molecular weight of the hydroxyl group containing acrylic resin		15000	18000	15000	2000

[0042]

<Examples 1 to 5 and Comparative Examples 1 to 8>

The clear paints CC-1 to CC-13 were prepared by mixing together successively the raw materials shown in Table 4 and Table 5 and stirring to provide uniform mixtures.

[0043]

Table 4

	Example 1	Example 2	Example 3	Example 4	Example 5
Clear Paint	CC-1	CC-2	CC-3	CC-4	CC-5
Hydroxyl group containing resin A-1	46.8	48.2	41.9		
Hydroxyl group containing resin A-2				52.0	48.2
Hydroxyl group containing resin A-3					
Hydroxyl group containing resin A-1					
Reactive diluent D-1	4.7				
Reactive diluent D-2		4.7			
Reactive diluent D-3			7.1		
Reactive diluent D-4				4.1	
Reactive diluent D-5					7.1
Reactive diluent D-6					
Reactive diluent D-7					
Reactive diluent D-8					
Reactive diluent D-9					
Crosslinking agent N3300 1)	19.1	17.8	21.4	14.8	15.6
Ultraviolet absorber 2)	2.0	2.0	2.0	2.0	2.0
Photo-stabilizer 3)	1.0	1.0	1.0	1.0	1.0
Surface controlling agent solution 4)	1.0	1.0	1.0	1.0	1.0
Diluting solvent 5)	25.4	25.3	25.7	25.0	25.1
Total	100.0	100.0	100.0	100.0	100.0
Hydroxyl group containing acrylic resin/reactive diluent resin mass ratio	90/10	90/10	85/15	92/8	85/15
Hydroxyl group value of the hydroxyl group containing acrylic resin (mgKOH/g)	140	140	140	100	100
Weight average molecular weight of the hydroxyl group containing acrylic resin	15000	15000	15000	18000	18000
NCO/OH functional group ratio	1.0	0.9	1.2	1.0	1.0
Hydroxyl group value of the reactive diluent (mgKOH/g)	175	184	144	125	162
Weight average molecular weight of the reactive diluent	1800	1800	1400	1500	1600
Proportion of caprolactone structural units included in the reactive diluent (mass%)	35.6	37.5	30.5	25.5	33.0
CHDM/TMP mol ratio	7/3	6/4	8/2	10/0	9/1

[0044]

Table 5

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex.5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex.8
Clear Paint	CC-6	CC-7	CC-8	CC-9	CC-10	CC-11	CC-12	CC-13
Hydroxyl group containing resin A-1	50.9	43.9	44.3	44.1	44.3	41.7		
Hydroxyl group containing resin A-2								
Hydroxyl group containing resin A-3							54.1	
Hydroxyl group containing resin A-1								43.1
Reactive diluent D-1	0.9					9.3	7.0	7.2
Reactive diluent D-2								
Reactive diluent D-3								
Reactive diluent D-4								
Reactive diluent D-5								
Reactive diluent D-6		9.5						
Reactive diluent D-7			7.1					
Reactive diluent D-8				5.7				
Reactive diluent D-9					6.2			
Crosslinking agent N3300 1)	18.8	17.4	19.2	20.6	20.1	19.5	9.6	19.3
Ultraviolet absorber 2)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Photo-stabilizer 3)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Surface controlling agent solution 4)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Diluting solvent 5)	25.4	25.2	25.4	25.5	25.5	25.5	25.3	26.4
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Hydroxyl group containing acrylic resin/reactive diluent resin mass ratio	98/2	82/18	85/15	90/10	88/12	82/18	88/12	85/15
Hydroxyl group value of the hydroxyl group containing acrylic resin (mgKOH/g)	140	140	140	140	140	140	40	140
Weight average molecular weight of the hydroxyl group containing acrylic resin	15000	15000	15000	15000	15000	15000	15000	2000
NCO/OH functional group ratio	1.0	1.0	1.0	1.2	1.0	1.0	1.0	1.0
Hydroxyl group value of the reactive diluent (mgKOH/g)	175	51	165	75	235	175	175	175
Weight average molecular weight of the reactive diluent	1800	1800	810	3200	1200	1800	1800	1800
Proportion of caprolactone structural units included in the reactive diluent (mass%)	35.6	10.3	33.6	15.1	47.7	35.6	35.6	35.6
CHDM/TMP mol ratio	7/3	10/0	8/2	7/3	0/10	7/3	7/3	7/3

[0045]

Notes for Table 4 and Table 5:

1) Crosslinking Agent N3300: Desmodur N3300, Trade name, a liquid HDI isocyanurate type resin (involatile fraction 100 mass%, NCO content 23 mass%), produced by the Sumika Bayer Urethane Co.

2) Ultraviolet absorber solution: A 20 mass% xylene solution of Tinuvin 900, trade name, produced by the Ciba Specialty Chemical Co.

3) Photo-stabilizer solution: A 20 mass% xylene solution of Tinuvin 292, trade name, produced by the Ciba Specialty Chemical Co.

4) Surface controlling agent solution: A 10 mass% xylene solution of BYK-300, trade name, produced by the Byk-Chemie Co.

5) Diluting Solvent: A 1 : 1 by mass solvent mixture of xylene/butyl acetate.

[0046]

<Sample Preparation and Investigation of Paint Film Performance>

Cationic electro-deposition paint Aqua No. 4200 (trade name, produced by the BASF Coatings Japan Co.) was electro-deposition painted onto a zinc phosphate treated mild steel sheet in such a way as to provide a dry film thickness of 20 μm and baked at 175°C for 25 minutes and then the mid-coat paint Hiepico No. 560 (trade name, produced by the BASF Coatings Japan Co.)

was air-spay painted on in such a way as to provide a dry film thickness of 30 μm and baked at 140°C for 30 minutes. Next Belcoat No.6000 Black (trade name, produced by the BASF Coatings Japan Co., color: black) which is a solvent-based base-coat paint was air spray painted in such a way as to provide a dry film thickness of 15 μm and, after setting for 3 minutes at 20°C, the abovementioned clear paints which had been diluted to the painting viscosity (25 seconds at 20°C, Ford Cup No.4) with Solvesso 100 (trade name, aromatic petroleum naphtha, produced by the Esso Co.) were air spray painted wet-on-wet in such a way as to provide a dry film thickness of 40 μm in each case and baked at 140°C for 30 minutes to prepare samples.

Moreover, with just the test sheets for staining resistance in all of the illustrative examples the base-coat paint used was switched to Belcoat No.6000 white (produced by the BASF Coatings Japan Co., color: white).

[0047]

The paint film performance of the test specimens obtained was evaluated with the methods of evaluation indicated below. The results are shown in Table 6 and Table 7.

(1) Paint Film Hardness

The paint film hardness was measured at 25°C using a Kernich oscillating probe hardness meter produced by

the Ericssen Co., and evaluation was carried out. The Kernich oscillating probe hardness meter measures the paint film hardness by establishing the tip of the vibrating probe on the paint film which has been arranged in the horizontal orientation and a higher hardness is indicated by a larger number of oscillations.

◎: 90 or more times

○: 80 or more times

Δ: 70 or more times

X: Less than 70 times

[0048]

(2) Car-wash Scratching Resistance

Muddy water (JIS Z-8901-84, Class 8 dust/water/neutral detergent mixed in a ratio by weight of 10/99/1) was coated with a brush on a test sheet and then subjected to 10 seconds rotation with a car-wash brush at 150 rpm in an automatic car-wash and the test sheet was rinsed with running water. After repeating this process twice the extent of scratching of the test sheet surface was determined by measuring the L* value with a color difference meter (trade name CR-331, produced by the Minolta Camera Co.). The ΔL* value was calculated by means of the equation indicated below and the car-wash scratching resistance was evaluated on the basis of this value.

ΔL* Value = L* value after the test - L* value before the test

◎: ΔL* value less than 1

○: ΔL* value 1 or more but less than 2

Δ: ΔL* value 2 or more but less than 3

X: ΔL* value 3 or more

[0049]

(3) Accelerated Weather Resistance

The 60° mirror surface gloss of the paint film was measured with a digital variable-angle gloss meter (produced by the Suga Shikenki Co.) after exposure for 1,000 hours using a xenon lamp type accelerated weather resistance tester (JIS K5600 7.7 (1999)) and the gloss retention rate was calculated by comparison with the initial gloss value.

○: Gloss retention rate at least 90%

Δ: Gloss retention rate at least 80% but less than 90%

X: Gloss retention rate less than 80%

[0050]

(4) Acid Resistance

A 40% sulfuric acid aqueous solution (0.2 ml) was located as a spot on a test sheet and heated to 60°C for 15 minutes and then rinsed off with water and the extent of formation of a staining mark was observed visually.

○: Virtually no change could be seen in the paint film.

Δ: A slight staining mark was seen in the paint film.

X: A pronounced staining mark was seen in the paint film.

[0051]

(5) Compatibility

Hydroxyl group containing acrylic resin (50 g) and 50 g of the reactive diluent were each weighed out in a beaker, 20 g of xylene were added and the mixture was stirred uniformly. Next, the mixed solution was placed on a transparent glass plate and, after being left to stand for 10 minutes in the perpendicular state, the transparency of the paint film on the glass plate was evaluated.

O: Transparent with no whitening

X: White cloudiness was seen

[0052]

Table 6

	Example 1	Example 2	Example 3	Example 4	Example 5
Paint film hardness	◎	○	○	○	○
Car-wash scratching resistance	◎	◎	◎	○	○
Accelerated weather resistance	○	○	○	○	○
Acid Resistance	○	○	○	○	○
Compatibility	○	○	○	○	○

[0053]

Table 7

	Comp. Ex. 1	Comp. Ex2	Comp. Ex.3	Comp. Ex.4	Comp. Ex.5	Comp. Ex.6	Comp. Ex.7	Comp. Ex.8
Paint film hardness	X	Δ	X	-	Δ	◎	X	X
Car-wash scratching resistance	○	Δ	○	-	○	X	X	○
Accelerated weather resistance	○	○	X	-	X	X	○	x
Acid Resistance	○	Δ	X	-	Δ	○	X	X
Compatibility	○	○	○	X	○	○	○	○

Claims

[Claim 1]

A reactive diluent comprising a hydroxyl group containing resin which has been obtained by reacting at the same time (a) a compound where two or more hydroxyl groups are included in one molecule, (b) a compound where two non-sulfur modified isocyanate groups are included in one molecule and (c) a lactone compound, characterized in that said hydroxyl group containing resin has a hydroxyl group value of from 100 to 200 mgK OH/g and a weight average molecular weight of from 1,000 to 2,000 and contains from 20 to 40 mass% of structural units based on the lactone compound of the (c) component.

[Claim 2]

A reactive diluent comprising a hydroxyl group containing resin which has been obtained by reacting (a) a compound where two or more hydroxyl groups are included in one molecule and (b) a compound where two non-sulfur modified isocyanate groups are included in one molecule and then carrying out an addition reaction of (c) a lactone compound, characterized in that said hydroxyl group containing resin has a hydroxyl group value of from 100 to 200 mgKOH/g and a weight average molecular weight of from 1,000 to 2,000 and contains from 20 to 40 mass% of structural units based on the

lactone compound of the (c) component.

[Claim 3]

A thermosetting paint composition, characterized in that it includes the reactive diluent claimed in claim 1 or claim 2, hydroxyl group containing acrylic resin which has a hydroxyl group value of from 80 to 150 mgKOH/g and a weight average molecular weight of from 3,000 to 100,000 and polyfunctional isocyanate compound and in which the proportion of the contents of said reactive diluent and said hydroxyl group containing acrylic resin as the resin mass ratio is within the range from 5/95 to 15/85.

[Claim 4]

The thermosetting paint composition claimed in claim 3 in which the polyfunctional isocyanate compound is an isocyanurate compound.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2008/001710

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G18/08 C08G18/12 C08G18/28 C08G18/32 C08G18/34
C08G18/62 C08G18/79 C08G18/80

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G

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 practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 199 28 687 A1 (BASF AG [DE]) 28 December 2000 (2000-12-28) example 2	1-4
A	GB 2 193 504 A (BASF CORP) 10 February 1988 (1988-02-10) examples 1-7	1-4
A	DE 197 23 895 A1 (LEE YOON JICK DIPL ING [DE]; SELIGER HARTMUT PROF DR ING [DE]) 10 December 1998 (1998-12-10) page 12, line 5 - line 56	1-4
A	WO 03/004544 A (RHONE POULENC CHIMIE [FR]; BERNARD JEAN-MARIE [FR]) 16 January 2003 (2003-01-16) example 8	1-4

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 October 2008	29/10/2008

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

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2008/001710

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 479 704 A (BAYER MATERIALSCIENCE AG [DE]) 24 November 2004 (2004-11-24) page 2, line 40 example 4, 2. column of the table on pages 16 and 17 -----	1-4

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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