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(54) Title: COATING COMPOSITION AND METHOD OF FORMING COATING FILM

(57) Abstract: A coating composition comprising (A) a hydroxyl group-containing resin with a hydroxyl value of 80-200 mgKOH/g and a weight-average molecular weight of 2500-40,000, (B) a polyisocyanate compound, and (C) a polycarbonate diol compound of number-average molecular weight 400-2500 with a viscosity of no greater than 10,000 mPa·s at 50°C obtained by reacting a C2-10 diol as the diol component with a carbonylating agent. It is thereby possible to provide cured coating films with excellent mar resistance, acid resistance, stain resistance and finished appearances.



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DESCRIPTION

COATING COMPOSITION AND METHOD OF FORMING COATING FILM5 Technical Field

The present invention relates to a coating composition that can obtain a coating film with excellent mar resistance, acid resistance, stain resistance and finished appearances, and to a method of forming a
10 coating film using the composition.

Background Art

Paints applied onto objects such as automobile bodies have been required to exhibit excellent film
15 performance including mar resistance, acid resistance, stain resistance and finished appearances.

Melamine crosslinked paints have been widely used in the prior art as paints for such objects. Melamine crosslinked paints comprise hydroxyl group-containing
20 resins and melamine resins as crosslinking agents, and because of their high crosslink density during heat curing, they excel in film performance such as mar resistance and finished appearances. Such paints, however, have problems in that the melamine crosslinked
25 bonds undergo hydrolysis in acid rain, such that the acid resistance of the coating films is inferior.

Japanese Unexamined Patent Publication HEI No. 6-220397 discloses a two-pack urethane crosslinked coating composition comprising a hydroxyl group-containing
30 acrylic resin, a hydroxyl group-containing oligoester and an isocyanate prepolymer. Because the urethane crosslinked bonds in the paint are resistant to hydrolysis, the coating film has excellent acid resistance. The mar resistance of the coating film,
35 however, is inadequate.

Disclosure of the Invention

An object of the present invention is to provide a coating composition that is capable of forming cured coating films having excellent mar resistance, acid resistance, stain resistance and finished appearances.

5 As a result of much extensive research conducted for solving the problems described above, the present inventors discovered that the problems can be solved by a coating composition comprising a hydroxyl group-
10 containing resin with a specific hydroxyl value and average molecular weight, a polyisocyanate compound and a polycarbonate diol compound having a viscosity and number-average molecular weight in specified ranges which is obtained by reacting a C2-10 diol as the diol component with a carbonylating agent, and the invention
15 has been completed upon the findings.

Specifically, the invention provides a coating composition comprising (A) a hydroxyl group-containing resin with a hydroxyl value of 80-200 mgKOH/g and a weight-average molecular weight of 2500-40,000, (B) a
20 polyisocyanate compound, and (C) a polycarbonate diol compound of number-average molecular weight 400-2500 with a viscosity of no greater than 10,000 mPa·s at 50°C, obtained by reacting a C2-10 diol as the diol component with a carbonylating agent.

25 The invention further provides a method of forming a multilayer coating film whereby a multilayer coating film is formed by applying at least one colored base coat paint and at least one clear coat paint in that order on an object, wherein the aforementioned coating composition
30 is applied as the uppermost clear coat paint layer.

Because of the high compatibility of the polycarbonate diol compound with the hydroxyl group-containing resin and polyisocyanate compound in the coating composition of the invention having this specific
35 constitution, coating films obtained therefrom have satisfactory finished appearances. Furthermore, since the physical properties of such coating films including

mechanical strength are enhanced by the polycarbonate diol compound, and the urethane crosslinked bonds and carbonate bonds produced by reaction between the hydroxyl group-containing resin and polyisocyanate compound are highly resistant to hydrolysis by acids, the cured coating films formed also exhibit excellent mar resistance, acid resistance and stain resistance.

Best Mode for Carrying Out the Invention

Preferred modes of the coating composition (hereinafter also referred to as "paint") and multilayer method of forming a coating film of the invention will now be explained, but it is to be understood that the invention is not limited to these modes, and various modifications may be implemented that are within the spirit and scope of the invention.

The coating composition of the invention is a coating composition comprising (A) a hydroxyl group-containing resin with a specific hydroxyl value and average molecular weight, (B) a polyisocyanate compound, and (C) a polycarbonate diol compound with a viscosity and number-average molecular weight in specified ranges, obtained by reacting a C2-10 diol as the diol component with a carbonylating agent.

Hydroxyl group-containing resin (A)

The hydroxyl group-containing resin (A) used in the coating composition of the invention is a hydroxyl group-containing resin with a hydroxyl value of 80-200 mgKOH/g and a weight-average molecular weight of 2500-40,000.

The hydroxyl group-containing resin (A) is not particularly restricted so long as the hydroxyl value is 80-200 mgKOH/g and the weight-average molecular weight is in the range of 2500-40,000, and as specific examples there may be mentioned acrylic resins, polyester resins, polyether resins, polyurethane resins and the like, among which hydroxyl group-containing acrylic resins, hydroxyl group-containing polyester resins and hydroxyl group-

containing polyurethane resins are preferred.

The hydroxyl group-containing acrylic resin may be produced by copolymerizing a hydroxyl group-containing unsaturated monomer (M-1) and another copolymerizable
5 unsaturated monomer (M-2) by an ordinary method.

The hydroxyl group-containing unsaturated monomer (M-1) is a compound with one hydroxyl group and one unsaturated bond in the molecule, where the hydroxyl group mainly acts as a functional group for reaction with
10 the crosslinking agent. As such monomers there are preferred monoesters of acrylic acid or methacrylic acid and C2-10 dihydric alcohols, and as specific examples there may be mentioned hydroxyalkyl (meth)acrylates such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl
15 (meth)acrylate, 3-hydroxypropyl (meth)acrylate and 4-hydroxybutyl (meth)acrylate. As monomers there may also be mentioned ring-opening polymerization addition products of the aforementioned hydroxyalkyl
(meth)acrylates and lactones such as ϵ -caprolactone. As
20 specific examples there may be mentioned "PLACCEL FA-1", "PLACCEL FA-2", "PLACCEL FA-3", "PLACCEL FA-4", "PLACCEL FA-5", "PLACCEL FM-1", "PLACCEL FM-2", "PLACCEL FM-3", "PLACCEL FM-4", "PLACCEL FM-5" (all trade names of Dical Chemical Industries, Ltd.).

25 Preferred among these from the standpoint of coating film mar resistance are hydroxyl group-containing unsaturated monomers (1a) with hydroxyl group-containing C4 or greater hydrocarbon groups. Using monomer (1a) as a component can yield a coating film with high crosslink
30 density, thus providing an effect of enhanced coating film mar resistance.

As examples of hydroxyl group-containing unsaturated monomers with hydroxyl group-containing C4 or greater hydrocarbon groups there may be mentioned compounds
35 obtained by ring-opening polymerization of ϵ -caprolactone with monoesters of acrylic acid or methacrylic acid and C4-10 dihydric alcohols or monoesters of acrylic acid or

methacrylic acid and C2-10 dihydric alcohols.

As a particularly preferred example of a monoester of acrylic acid or methacrylic acid and a C4-10 dihydric alcohol there may be mentioned 4-hydroxybutyl (meth)acrylate.

As particularly preferred examples of compounds obtained by ring-opening polymerization of ϵ -caprolactone with a monoester of acrylic acid or methacrylic acid and a C2-10 dihydric alcohol, there may be mentioned "PLACCEL FA-2" and "PLACCEL FM-3".

From the viewpoint of improving the mar resistance without lowering the acid resistance of the coating film it is preferred to use an unsaturated monomer comprising both a cyclohexyl ring and a hydroxyl group, and specifically there may be mentioned CHDMMA (1,4-cyclohexanedimethanol monoacrylate, product of Nippon Kasei Chemical Co., Ltd.).

As unsaturated monomers comprising both a cyclohexyl ring and a hydroxyl group there may be used macromonomers obtained by reacting a polyester oligomer having a hydroxycyclohexyl or methylolcyclohexyl group at both ends of the molecule with the reaction product of a diisocyanate compound and a hydroxyl group-containing (meth)acrylate (equimolar). As examples of polyester oligomers there may be mentioned FLEXORES 148 and FLEXORES 188 (both products of King Industries, US).

An acrylic resin comprising both a cyclohexyl ring and hydroxyl group, obtained using an unsaturated monomer with both a cyclohexyl ring and hydroxyl group as copolymerizing components, may be obtained by, for example, a process involving addition reaction of a hydroxyl group-containing acrylic resin and a cyclohexyl ring-containing acid anhydride (for example, hexahydrophthalic anhydride), followed by acid/epoxy reaction of an epoxy group- and hydroxyl group-containing compound (for example, glycidol) with the carboxylic acid produced by the addition reaction, for further addition

reaction to produce terminal hydroxyl groups.

The proportion of the hydroxyl group-containing unsaturated monomer (M-1) is preferably in the range of 20-50 mass% and especially 25-45 mass% based on the total weight of the monomer mixture.

If the proportion of the hydroxyl group-containing unsaturated monomer (M-1) is less than 20 mass%, crosslinking of the cured coating film will be insufficient, often making it impossible to achieve the desired mar resistance. If it is greater than 50 mass%, on the other hand, compatibility and copolymerizing reactivity with the other copolymerizable unsaturated monomer (M-2) will be reduced and compatibility of the obtained hydroxyl group-containing acrylic resin with the other components (polyisocyanate compound (B) and polycarbonate diol compound (C)) will be reduced, thereby potentially impairing the finished appearance of the coating film.

Throughout the present specification, "(meth)acrylate" refers to "acrylate" or "methacrylate".

The other copolymerizable unsaturated monomer (M-2) is a compound having one unsaturated bond in the molecule, other than the above-mentioned hydroxyl group-containing unsaturated monomer (M-1), and specific examples thereof are listed below as (1) - (8).

(1) Acid group-containing unsaturated monomers: Compounds having one or more acid groups and one unsaturated bond in the molecule, e.g. carboxyl-containing unsaturated monomers such as (meth)acrylic acid, crotonic acid, itaconic acid, maleic acid and maleic anhydride; sulfonic acid-containing unsaturated monomers such as vinylsulfonic acid and sulfoethyl (meth)acrylate, and acidic phosphoric acid ester-based unsaturated monomers such as 2-(meth)acryloyloxyethyl acid phosphate, 2-(meth)acryloyloxypropyl acid phosphate, 2-(meth)acryloyloxy-3-chloropropyl acid phosphate and 2-methacryloyloxyethylphenylphosphoric acid.

These may be used alone or in combinations of two or more.

For these acid group-containing unsaturated monomers, component (A) can function as an internal catalyst for crosslinking reaction with the crosslinking agent, and they are preferably used in a range of 0-5 mass% and especially 0.1-3 mass% based on the total weight of the monomer mixture of the hydroxyl group-containing acrylic resin.

(2) Monoesters of acrylic acid or methacrylic acid with C1-20 monohydric alcohol: Examples include methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, n-butyl (meth)acrylate, iso-butyl (meth)acrylate, tert-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isooctyl (meth)acrylate, isomyristyl (meth)acrylate and isostearyl acrylate (trade names of Osaka Organic Chemical Industry, Ltd.), and cyclohexyl (meth)acrylate, lauryl (meth)acrylate, isobornyl (meth)acrylate, tricyclodecanyl (meth)acrylate, adamantyl (meth)acrylate, 3,5-dimethyladamantyl (meth)acrylate, 3-tetracyclododecyl methacrylate, tridecyl (meth)acrylate, stearyl (meth)acrylate, 4-methylcyclohexylmethyl (meth)acrylate, 4-ethylcyclohexylmethyl (meth)acrylate, 4-methoxycyclohexylmethyl (meth)acrylate, tert-butylcyclohexyl (meth)acrylate, cyclooctyl (meth)acrylate, cyclododecyl (meth)acrylate and tetrahydrofurfuryl (meth)acrylate.

Preferred among these from the standpoint of enhancing the coating film stain resistance are (2a) unsaturated monomers with C10-20 bridged alicyclic hydrocarbon groups and/or unsaturated monomers with C3-12 alicyclic hydrocarbon groups. By including monomer (2a) as a constituent component, it is possible to increase the Tg and reduce the polarity of the obtained resin, thereby enhancing the finished appearances by smoothing of the surface, and also increasing the water resistance and stain resistance.

As typical examples of C10-20 bridged alicyclic hydrocarbon groups there may be mentioned isobornyl, tricyclodecanyl and adamantyl.

As specific examples of unsaturated monomers with C10-20 bridged alicyclic hydrocarbon groups there may be mentioned isobornyl (meth)acrylate, tricyclodecanyl (meth)acrylate, adamantyl (meth)acrylate, 3,5-dimethyladamantyl (meth)acrylate and 3-tetracyclododecyl methacrylate.

As specific examples of unsaturated monomers with C3-12 alicyclic hydrocarbon groups there may be mentioned cyclohexyl (meth)acrylate, 4-methylcyclohexylmethyl (meth)acrylate, 4-ethylcyclohexylmethyl (meth)acrylate, 4-methoxycyclohexylmethyl (meth)acrylate, tert-butylcyclohexyl (meth)acrylate, cyclooctyl (meth)acrylate, cyclododecyl (meth)acrylate and tetrahydrofurfuryl (meth)acrylate.

When monomer (2a) is a constituent component, the proportion is in the range of preferably 3-50 mass% and especially 10-40 mass% based on the total weight of the monomer mixture.

Of those mentioned above, unsaturated monomers (2b) having a C8 or greater hydrocarbon group with a branched structure are preferably used from the standpoint of enhancing the coating film mar resistance. By including monomer (2b) as a constituent component, it is possible to lower the Tg and polarity of the obtained resin, thereby enhancing the coating film mar resistance by imparting flexibility, and improving the finished appearances by smoothing of the surface. Using a branched structure can inhibit lowering of the Tg of the coating film compared to using an unsaturated monomer with a linear C8 or greater hydrocarbon group as the constituent component, and is therefore advantageous from the standpoint of improving the acid resistance.

Specific examples of unsaturated monomers with branched C8 or greater hydrocarbon groups among those

mentioned above include 2-ethylhexyl acrylate, isooctyl (meth)acrylate, isomyristyl (meth)acrylate and isostearyl acrylate (products of Osaka Organic Chemical Industry, Ltd.).

5 When monomer (2b) is a constituent component, the proportion is in the range of preferably 3-50 mass% and especially 10-40 mass% based on the total weight of the monomer mixture.

10 (3) Alkoxysilane group-containing unsaturated monomers: For example, vinyltrimethoxysilane, vinyltriethoxysilane, acryloxyethyltrimethoxysilane, methacryloxyethyltrimethoxysilane, acryloxypropyltrimethoxysilane, methacryloxypropyltrimethoxysilane, 15 acryloxypropyltriethoxysilane, methacryloxypropyltriethoxysilane and vinyltris(β -methoxyethoxy)silane.

 Preferred among these alkoxysilane group-containing unsaturated monomers are vinyltrimethoxysilane, γ - 20 acryloxypropyltrimethoxysilane and γ -methacryloxypropyltrimethoxysilane.

 By using an alkoxysilane group-containing unsaturated monomer as a constituent component, it is possible to produce a crosslinked bond by condensation 25 reaction between the alkoxysilane groups and reaction between the alkoxysilane groups and hydroxyl groups, in addition to the crosslinked bonds between the hydroxyl and isocyanate groups. This can increase the crosslink density of the obtained coating film, thereby enhancing 30 the acid resistance and stain resistance.

 When an alkoxysilane group-containing unsaturated monomer is used as a constituent component, the proportion is preferably in the range of 3-50 mass% and especially in the range of 5-35 mass%, based on the total 35 weight of the monomer mixture.

 (4) Aromatic unsaturated monomers: For example

styrene, α -methylstyrene and vinyltoluene.

Using an aromatic unsaturated monomer as a constituent component can increase the Tg of the obtained resin and yield a hydrophobic coating film with a high refractive index, thereby producing an effect of enhanced finished appearances by improved gloss of the coating film, and of increased water resistance and acid resistance.

When an aromatic unsaturated monomer is used as a constituent component, the proportion is preferably in the range of 3-50 mass% and especially in the range of 5-40 mass%, based on the total weight of the monomer mixture.

(5) Glycidyl group-containing unsaturated monomers: Compounds having one glycidyl group and one unsaturated bond in the molecule, such as glycidyl acrylate and glycidyl methacrylate.

(6) Nitrogen-containing unsaturated monomers: For example, (meth)acrylamide, dimethylacrylamide, N,N-dimethylpropylacrylamide, N-butoxymethylacrylamide, N-methylolacrylamide, N-methylolmethacrylamide, diacetoneacrylamide, N,N-dimethylaminoethyl (meth)acrylate, vinylpyridine and vinylimidazole.

(7) Other vinyl compounds: For example, vinyl acetate, vinyl propionate, vinyl chloride, and the versatic acid vinyl esters VEOVA 9 and VEOVA 10 (trade names of Japan Epoxy Resins Co., Ltd.).

(8) Unsaturated bond-containing nitrile-based compounds: For example, acrylonitrile and methacrylonitrile.

These unsaturated monomer (M-2) compounds may be used alone or in combinations of two or more.

Monomer mixtures composed of these monomers (M-1) and (M-2) may be copolymerized to obtain hydroxyl group-containing acrylic resins.

As particularly preferred hydroxyl group-containing acrylic resins that yield coating compositions with

excellent film performance including mar resistance, acid resistance and stain resistance, as well as excellent coating film finished appearances, there may be mentioned hydroxyl group-containing acrylic resins obtained by copolymerization of monomer mixtures comprising monomers (M-1) and (M-2) with the following compositions.

1. A hydroxyl group-containing acrylic resin (α) obtained by copolymerizing a monomer mixture comprising (A) 3-40 mass% of an aromatic unsaturated monomer and/or an unsaturated monomer with a C3-12 alicyclic hydrocarbon group, (B) 3-40 mass% of an unsaturated monomer with a C10-20 bridged alicyclic hydrocarbon group, (C) 20-50 mass% of a hydroxyl group-containing unsaturated monomer and (D) 0-60 mass% of another copolymerizable unsaturated monomer, wherein the total weight of components (A) and (B) is 20-70 parts by mass with respect to 100 parts by mass of the monomer mixture.

2. A hydroxyl group-containing acrylic resin (β) obtained by copolymerizing a monomer mixture comprising (A) 3-40 mass% of an aromatic unsaturated monomer and/or an unsaturated monomer with a C3-12 alicyclic hydrocarbon group, (B) 3-40 mass% of an unsaturated monomer with a C8 or greater branched alicyclic hydrocarbon group, (C) 3-50 mass% of a hydroxyl group-containing unsaturated monomer with a C4 or greater hydroxyl group-containing hydrocarbon group and (D) 0-77 mass% of another copolymerizable unsaturated monomer, wherein the total weight of components (A) and (B) is 20-70 parts by mass with respect to 100 parts by mass of the monomer mixture.

The method of copolymerizing the aforementioned monomer mixture to obtain the hydroxyl group-containing acrylic resin is not particularly restricted and any known copolymerization method may be used, but most preferred is a solution polymerization process wherein polymerization is conducted in an organic solvent in the presence of a polymerization initiator.

As examples of organic solvents to be used for

solution polymerization there may be mentioned aromatic solvents such as toluene, xylene and SWASOL 1000 (high boiling point petroleum-based solvent by Cosmo Oil Co., Ltd.); ester-based solvents such as ethyl acetate, 3-methoxybutyl acetate, ethyleneglycol ethyl ether acetate and propyleneglycol methyl ether acetate; ketone-based solvents such as methyl ethyl ketone, methyl isobutyl ketone and methyl amyl ketone, and propyl propionate, butyl propionate, ethoxyethyl propionate and the like.

10 These organic solvents may be used alone or in combinations of two or more, but since the hydroxyl group-containing acrylic resin used in the paint has a high hydroxyl value, a high boiling point ester-based solvent or ketone-based solvent is preferably used from the viewpoint of resin solubility. High boiling point aromatic solvents may also be used in appropriate combinations.

 As examples of polymerization initiators to be used for copolymerization of the hydroxyl group-containing acrylic resin there may be mentioned 2,2'-azobisisobutyronitrile, benzoyl peroxide, di-t-butyl peroxide, di-t-amyl peroxide, t-butyl peroctoate, 2,2'-azobis(2-methylbutyronitrile) and the like, which are known as radical polymerization initiators.

25 The hydroxyl value of the hydroxyl group-containing acrylic resin is in the range of 80-200 mgKOH/g, and preferably in the range of 100-170 mgKOH/g. A hydroxyl value of less than 80 mgKOH/g will result in low crosslink density, possibly leading to insufficient mar resistance. A value exceeding 200 mgKOH/g may lower the water resistance of the coating film.

 The weight-average molecular weight of the hydroxyl group-containing acrylic resin is in the range of 2500-40,000 and preferably in the range of 5000-30,000. A weight-average molecular weight of less than 2500 may lower the film performance including acid resistance, while greater than 40,000 may reduce the smoothness of

the coating film, resulting in impaired finished appearances.

Throughout the present specification, the weight-average molecular weight is the value calculated from a chromatogram measured by gel permeation chromatography based on the molecular weight of standard polystyrene. An HLC8120GPC apparatus (product of Tosoh Corp.) was used for the gel permeation chromatography. Four columns, "TSKgel G-4000HXL", "TSKgel G-3000HXL", "TSKgel G-2500HXL" and "TSKgel G-2000HXL" (all products of Tosoh Corp.) were used; Mobile phase: tetrahydrofuran, Measuring temperature: 40°C, Flow rate: 1 cc/min, Detector: RI.

The glass transition temperature of the hydroxyl group-containing acrylic resin is preferably in the range of -40°C to 85°C, and more preferably in the range of -30°C to 80°C. A glass transition temperature of below -40°C may result in insufficient coating film hardness, while above 85°C may lead to reduced surface smoothness of the coating film.

A hydroxyl group-containing polyester resin to be used as the hydroxyl group-containing resin (A) may be produced by esterification reaction of a polybasic acid and a polyhydric alcohol by an ordinary process. The polybasic acid is a compound having two or more carboxyl groups in the molecule, examples of which include phthalic acid, isophthalic acid, terephthalic acid, succinic acid, adipic acid, azelaic acid, sebacic acid, tetrahydrophthalic acid, hexahydrophthalic acid, maleic acid, fumaric acid, itaconic acid, trimellitic acid, pyromellitic acid and their anhydrides, while a polyhydric alcohol is a compound having two or more hydroxyl groups in the molecule, examples of which include diols such as ethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2-diethyl-1,3-propanediol, neopentylglycol,

1,9-nonanediol, 1,4-cyclohexanediol,
hydroxypivaneopentylglycol phosphate ester, 2-butyl-2-
ethyl-1,3-propanediol, 3-methyl-1,5-pentanediol, 2,2,4-
trimethylpentanediol and bisphenol hydride A, trihydric
5 and greater polyols such as trimethylolpropane,
trimethylolethane, glycerin and pentaerythritol, and
hydroxycarboxylic acids such as 2,2-dimethylolpropionic
acid, 2,2-dimethylolbutanoic acid, 2,2-
dimethylolpentanoic acid, 2,2-dimethylolhexanoic acid and
10 2,2-dimethyloloctanoic acid.

Such compounds may be introduced into a polyester
resin by reacting an acid with an α -olefin epoxide such
as propylene oxide or butylene oxide, or a monoepoxy
compound such as CARDURA E10 (synthetic highly branched
15 saturated fatty acid glycidyl ester, trade name of Japan
Epoxy Resins Co., Ltd.).

For introduction of a carboxyl group into the
polyester resin, a carboxylic anhydride may be added to a
hydroxyl group-containing polyester to produce a half
20 ester.

The hydroxyl value of the hydroxyl group-containing
polyester resin is in the range of 80-200 mgKOH/g and
preferably in the range of 100-170 mgKOH/g. If the
hydroxyl value is less than 80 mgKOH/g the mar resistance
25 may be insufficient, and if it exceeds 200 mgKOH/g the
coating film water resistance may be reduced.

The weight-average molecular weight of the hydroxyl
group-containing polyester resin is in the range of 2500-
40,000 and preferably in the range of 5000-30,000. A
30 weight-average molecular weight of less than 2500 may
lower the film performance including acid resistance,
while greater than 40,000 may reduce the smoothness of
the coating film.

The glass transition temperature of the hydroxyl
35 group-containing polyester resin is preferably -40°C to
 85°C and more preferably -30°C to 80°C . A glass

transition temperature of below -40°C may result in insufficient coating film hardness, while above 85°C may lead to reduced surface smoothness of the coating film.

The scope of the hydroxyl group-containing resin (A) also includes urethane-modified acrylic resins and urethane-modified polyester resins.

As hydroxyl group-containing polyurethane resins there may be mentioned hydroxyl group-containing polyurethane resins obtained by reaction of polyols and polyisocyanates.

As examples of polyols there may be mentioned low molecular weight compounds such as ethylene glycol, diethylene glycol, propylene glycol, butyleneglycol, hexamethylene glycol and other dihydric alcohols, as well as trihydric alcohols such as trimethylolpropane, glycerin and pentaerythritol. As high molecular weight compounds there may be mentioned polyether polyols, polyester polyols, acryl polyols and epoxy polyols. As polyether polyols there may be mentioned polyethylene glycol, polypropylene glycol and polytetramethylene glycol. As polyester polyols there may be mentioned condensation products of alcohols such as dihydric alcohol, dipropylene glycol, 1,4-butanediol, 1,6-hexanediol and neopentyl glycol with dibasic acids such as adipic acid, azelaic acid and sebacic acid, lactone-based ring-opening polymer polyols such as polycaprolactone, and polycarbonate diols. For example, there may be used carboxyl group-containing polyols such as 2,2-dimethylolpropionic acid and 2,2-dimethylolbutanoic acid.

As examples of polyisocyanates to be reacted with the aforementioned polyols there may be mentioned aliphatic polyisocyanates such as hexamethylene diisocyanate, trimethylhexamethylene diisocyanate dimer acid diisocyanate and lysine diisocyanate, as well as biuret addition products and isocyanurate ring addition products of these polyisocyanates; alicyclic

diisocyanates such as isophorone diisocyanate, 4,4'-methylenebis(cyclohexyl isocyanate), methylcyclohexane-2,4-(or -2,6-)diisocyanate, 1,3-(or 1,4-)di(isocyanatomethyl)cyclohexane, 1,4-cyclohexane diisocyanate, 1,3-cyclopentane diisocyanate and 1,2-cyclohexane diisocyanate, as well as biuret addition products and isocyanurate ring addition products of these polyisocyanates; aromatic diisocyanate compounds such as xylylene diisocyanate, metaxylylene diisocyanate, tetramethylxylylene diisocyanate, tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 1,5-naphthalene diisocyanate, 1,4-naphthalene diisocyanate, 4,4-toluidine diisocyanate, 4,4'-diphenyl ether diisocyanate, (m- or p-)phenylene diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate, bis(4-isocyanatophenyl)sulfone and isopropylidenebis(4-phenyl isocyanate), as well as biuret addition products and isocyanurate ring addition products of these polyisocyanates; and polyisocyanates with three or more isocyanate groups in the molecule such as triphenylmethane-4,4',4''-triisocyanate, 1,3,5-triisocyanatobenzene, 2,4,6-triisocyanatotoluene and 4,4'-dimethyldiphenylmethane-2,2',5,5'-tetraisocyanate, as well as biuret addition products and isocyanurate ring addition products of these polyisocyanates.

The hydroxyl value of the hydroxyl group-containing polyurethane resin is in the range of 80-200 mgKOH/g and preferably in the range of 100-170 mgKOH/g. If the hydroxyl value is less than 80 mgKOH/g the mar resistance may be insufficient, and if it exceeds 200 mgKOH/g the coating film water resistance may be reduced.

The weight-average molecular weight of the hydroxyl group-containing polyurethane resin is in the range of 2500-40,000 and preferably in the range of 5000-30,000. A weight-average molecular weight of less than 2500 may lower the film performance including acid resistance, while greater than 40,000 may reduce the surface

smoothness of the coating film.

The glass transition temperature of the hydroxyl group-containing polyurethane resin is preferably in the range of -40°C to 85°C and more preferably in the range of -30°C to 80°C. A glass transition temperature of below -40°C may result in insufficient coating film hardness, while above 85°C may lead to reduced surface smoothness of the coating film.

Any of these examples for the hydroxyl group-containing resin (A) may be used alone or in combinations of two or more, but preferably hydroxyl group-containing acrylic resins or hydroxyl group-containing polyester resins are used as the hydroxyl group-containing resin (A).

Polyisocyanate compound (B)

The polyisocyanate compound (B) used in the coating composition of the invention is a compound with two or more free isocyanate groups in the molecule, and any one employed in the prior art for production of polyurethanes may be used. As examples there may be mentioned aliphatic polyisocyanates, alicyclic polyisocyanates, aromatic/aliphatic polyisocyanates, aromatic polyisocyanates and derivatives of these polyisocyanates.

As examples of aliphatic polyisocyanates there may be mentioned aliphatic diisocyanates such as trimethylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, pentamethylene diisocyanate, 1,2-propylene diisocyanate, 1,2-butylene diisocyanate, 2,3-butylene diisocyanate, 1,3-butylene diisocyanate, 2,4,4- or 2,2,4-trimethylhexamethylene diisocyanate and 2,6-diisocyanatomethyl caproate, and aliphatic triisocyanates such as lysine ester triisocyanate, 1,4,8-triisocyanatooctane, 1,6,11-triisocyanatoundecane, 1,8-diisocyanato-4-isocyanatomethyloctane, 1,3,6-triisocyanatohexane and 2,5,7-trimethyl-1,8-diisocyanato-5-isocyanatomethyloctane.

As examples of alicyclic polyisocyanates alicyclic diisocyanates such as 1,3-cyclopentene diisocyanate, 1,4-cyclohexane diisocyanate, 1,3-cyclohexane diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (common name: isophorone diisocyanate), 4,4'-methylenebis(cyclohexyl isocyanate), methyl-2,4-cyclohexane diisocyanate, methyl-2,6-cyclohexane diisocyanate, 1,3- or 1,4-bis(isocyanatomethyl)cyclohexane (common name: hydrogenated xylylene diisocyanate) or its mixtures, and norbornane diisocyanate, and alicyclic triisocyanates such as 1,3,5-triisocyanatocyclohexane, 1,3,5-trimethylisocyanatocyclohexane, 2-(3-isocyanatopropyl)-2,5-di(isocyanatomethyl)-bicyclo(2.2.1)heptane, 2-(3-isocyanatopropyl)-2,6-di(isocyanatomethyl)-bicyclo(2.2.1)heptane, 3-(3-isocyanatopropyl)-2,5-di(isocyanatomethyl)-bicyclo(2.2.1)heptane, 5-(2-isocyanatoethyl)-2-isocyanatomethyl-3-(3-isocyanatopropyl)-bicyclo(2.2.1)heptane, 6-(2-isocyanatoethyl)-2-isocyanatomethyl-3-(3-isocyanatopropyl)-bicyclo(2.2.1)heptane, 5-(2-isocyanatoethyl)-2-isocyanatomethyl-2-(3-isocyanatopropyl)-bicyclo(2.2.1)-heptane and 6-(2-isocyanatoethyl)-2-isocyanatomethyl-2-(3-isocyanatopropyl)-bicyclo(2.2.1)heptane.

As examples of aromatic/aliphatic polyisocyanates there may be mentioned aromatic/aliphatic diisocyanates such as 1,3- or 1,4-xylylene diisocyanate or mixtures thereof, ω,ω' -diisocyanato-1,4-diethylbenzene and 1,3- or 1,4-bis(1-isocyanato-1-methylethyl)benzene (common name: tetramethylxylylene diisocyanate) or mixtures thereof, and aromatic/aliphatic triisocyanates such as 1,3,5-triisocyanatomethylbenzene.

As examples of aromatic polyisocyanates there may be mentioned aromatic diisocyanates such as m-phenylene diisocyanate, p-phenylene diisocyanate, 4,4'-diphenyl diisocyanate, 1,5-naphthalene diisocyanate, 2,4'- or

4,4'-diphenylmethane diisocyanate or mixtures thereof,
2,4- or 2,6-tolylene diisocyanate or mixtures thereof,
4,4'-toluidine diisocyanate and 4,4'-diphenyl ether
diisocyanate, aromatic triisocyanates such as
5 triphenylmethane-4,4',4''-triisocyanate, 1,3,5-
triisocyanatobenzene and 2,4,6-triisocyanatotoluene, and
aromatic tetraisocyanates such as 4,4'-diphenylmethane-
2,2',5,5'-tetraisocyanate.

As examples of polyisocyanate derivatives there may
10 be mentioned dimers, trimers, biurets, allophanates,
carbodiimides, urethodiones, urethoimines, isocyanurates,
oxadiazinetriones, polymethylenepolyphenyl
polyisocyanates (crude MDIs, polymeric MDIs) and crude
TDIs of the aforementioned polyisocyanate compounds.

15 These polyisocyanate compounds may be used alone or
in combinations of two or more. Among these
polyisocyanate compounds, aliphatic diisocyanates and
their derivatives are most preferred from the standpoint
of mar resistance and weather resistance.

20 As polyisocyanate compounds there may also be used
blocked polyisocyanate compounds which are polyisocyanate
compounds with two or more free isocyanate groups in the
molecule wherein the isocyanate groups are blocked with a
blocking agent.

25 The blocking agent is any one that blocks free
isocyanate groups. The blocked polyisocyanate compound
regenerates isocyanate groups by heating at 100°C or
higher and preferably 130°C or higher, for ready reaction
with hydroxyl groups. As examples of such blocking
30 agents there may be mentioned phenol-based compounds such
as phenol, cresol, xylenol, nitrophenol, ethylphenol,
hydroxydiphenyl, butylphenol, isopropylphenol,
nonylphenol, octylphenol and hydroxymethyl benzoate;
lactam-based compounds such as ϵ -caprolactam, δ -
35 valerolactam, γ -butyrolactam and β -propiolactam; aliphatic
alcohol-based compounds such as methanol, ethanol, propyl

alcohol, butyl alcohol, amyl alcohol and lauryl alcohol;
ether-based compounds such as ethyleneglycol monomethyl
ether, ethyleneglycol monoethyl ether, ethyleneglycol
monobutyl ether, diethyleneglycol monomethyl ether,
5 diethyleneglycol monoethyl ether, propyleneglycol
monomethyl ether and methoxymethanol; glycolic acid
esters such as benzyl alcohol, glycolic acid, methyl
glycolate, ethyl glycolate and butyl glycolate; lactic
acid esters such as lactic acid, methyl lactate, ethyl
10 lactate and butyl lactate; alcohol-based compounds such
as methylol urea, methylolmelamine, diacetone alcohol, 2-
hydroxyethyl acrylate and 2-hydroxyethyl methacrylate;
oxime-based compounds such as formamideoxime,
acetamideoxime, acetooxime, methylethylketooxime,
15 diacetylmonooxime, benzophenoneoxime and
cyclohexaneoxime; active methylene-based compounds such
as dimethyl malonate, diethyl malonate, ethyl
acetoacetate, methyl acetoacetate and acetylacetone;
mercaptane-based compounds such as butylmercaptane, t-
20 butylmercaptane, hexylmercaptane, t-dodecylmercaptane, 2-
mercaptobenzothiazole, thiophenol, methylthiophenol and
ethylthiophenol; acid amide-based compounds such as
acetoanilide, acetanisidide, acetotoluide, acrylamide,
methacrylamide, acetic acid amide, stearic acid and
25 benzamide; imide-based compounds such as succinic acid
imide, phthalic acid imide and maleic acid imide; amine-
based compounds such as diphenylamine,
phenylnaphthylamine, xylidine, N-phenylxylidine,
carbazole, aniline, naphthylamine, butylamine,
30 dibutylamine and butylphenylamine; imidazole-based
compounds such as imidazole and 2-ethylimidazole;
pyrazole-based compounds such as 3,5-dimethylpyrazole;
urea-based compounds such as urea, thiourea,
ethyleneurea, ethylenethiourea and diphenylurea; carbamic
35 acid ester-based compounds such as phenyl N-
phenylcarbaminatate; imine-based compounds such as
ethyleneimine and propyleneimine; and sulfurous acid

salt-based compounds such as sodium bisulfite and potassium bisulfite.

5 A solvent may also be added as necessary for blocking (reaction with a blocking agent). The solvent used for the blocking reaction may be one that does not react with isocyanate groups, and as examples there may be mentioned ketones such as acetone and methyl ethyl ketone, esters such as ethyl acetate and other solvents such as N-methylpyrrolidone (NMP).

10 Any of these compounds for polyisocyanate compound (B) may be used alone or in combinations of two or more. Polycarbonate diol compound (C)

15 The polycarbonate diol compound (C) used in the coating composition of the invention is a polycarbonate diol compound with a viscosity of no greater than 10,000 mPa·s at 50°C and a number-average molecular weight of 400-2500, obtained by reacting a C2-10 diol as the diol component with a carbonylating agent.

20 A polycarbonate diol compound is usually obtained by polycondensation of a diol in the presence of a carbonylating agent.

The diol used in the polycarbonate diol compound is a C2-10 and preferably C4-8 dihydric alcohol. As specific examples there may be mentioned aliphatic diols such as 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 2-ethyl-1,6-hexanediol, 2-methyl-1,3-propanediol, 3-methyl-1,5-pentanediol and neopentyl glycol; alicyclic diols such as 1,3-cyclohexanediol, 1,4-cyclohexanediol and 1,4-cyclohexanedimethanol; aromatic diols such as p-xylenediol and p-tetrachloroxylenediol; and diols such as diethylene glycol and dipropylene glycol. These diols may be used alone or in combinations of two or more.

35 According to the invention, 1,6-hexanediol is preferably used as the diol component in the polycarbonate diol compound (C), from the viewpoint of

coating film durability and hardness.

Particularly preferred are two or more diol components with 1,6-hexanediol as the essential diol component, and specifically there may be mentioned
5 polycarbonate diol compounds obtained by reacting the two diol components 1,6-hexanediol and 1,5-pentanediol, 1,6-hexanediol and 1,4-butanediol or 1,6-hexanediol and 1,4-cyclohexanedimethanol.

As examples of commonly used carbonylating agents
10 there may be mentioned alkylene carbonate, dialkylcarbonate, diallylcarbonate and phosgene. Preferred among these are ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, dibutyl carbonate and diphenyl carbonate.

15 The polycarbonate diol compound may be synthesized by transesterification of the aforementioned carbonylating agent and diol compound in the presence or in the absence of a transesterification catalyst.

The polycarbonate diol compound (C) used for the
20 invention is a polycarbonate diol compound with a viscosity of no greater than 10,000 mPa·s at 50°C and a number-average molecular weight of 400-2500. It is important for the viscosity of the polycarbonate diol compound in the paint to be no greater than 10,000 mPa·s
25 at 50°C, because a viscosity exceeding 10,000 mPa·s at 50°C, even when the number-average molecular weight is in the range of 400-2500, can impair manageability and result in poor compatibility between the hydroxyl group-containing resin (A) and polyisocyanate compound (B),
30 thus producing reduced gloss or creating opacity in the coating film, and causing the coating film to have undesirable finished appearances.

The viscosity of the polycarbonate diol compound (C) is no greater than 10,000 mPa·s, preferably no greater
35 than 8000 mPa·s and even more preferably no greater than 5000 mPa·s at 50°C. The viscosity referred to here is the

value measured using a Brookfield viscometer under conditions of 50°C, 6 rpm.

The number-average molecular weight of the polycarbonate diol compound (C) is in the range of 400-
5 2500, preferably 500-2000 and even more preferably 800-1500.

The number-average molecular weight is the value calculated from a chromatogram measured by gel permeation chromatography based on the molecular weight of standard
10 polystyrene. An HLC8120GPC apparatus (product of Tosoh Corp.) was used for the gel permeation chromatography. Four columns, "TSKgel G-4000HXL", "TSKgel G-3000HXL", "TSKgel G-2500HXL" and "TSKgel G-2000HXL" (all products of Tosoh Corp.) were used; Mobile phase: tetrahydrofuran,
15 Measuring temperature: 40°C, Flow rate: 1 cc/min, Detector: RI.

A number-average molecular weight of less than 400 may reduce the mar resistance, hardness and weather resistance of the coating film. A number-average
20 molecular weight of greater than 2500 may lower compatibility between the hydroxyl group-containing resin (A) and polyisocyanate compound (B), and impair the finished appearances.

The hydroxyl value of the polycarbonate diol compound (C) is preferably 45-280 mgKOH/g and more
25 preferably 55-225 mgKOH/g. A hydroxyl value of less than 45 may reduce the mar resistance, hardness and weather resistance of the coating film, while a value of greater than 280 may reduce the finished appearances, mar
30 resistance and weather resistance of the coating film.

The polycarbonate diol compound (C) used may be a commercially available product. As examples of commercially available products there may be mentioned T-
5650J (diol components: 1,6-hexanediol and 1,5-
35 pentanediol), T-4671 and T-4672 (diol components: 1,6-hexanediol and 1,4-butanediol), by Asahi Kasei Corp.; and UM-CARB90 (diol components: 1,6-hexanediol and 1,4-

cyclohexanedimethanol), by Ube Industries, Ltd.

From the standpoint of the curing property and mar
resistance of the coating film, the equivalent ratio of
isocyanate groups in the polyisocyanate compound (B) to
5 hydroxyl groups in the hydroxyl group-containing resin
(A) and polycarbonate diol compound (C) (NCO/OH) in the
coating composition of the invention is in the range of
preferably 0.5-2.0 and more preferably 0.8-1.5.

The amounts of the hydroxyl group-containing resin
10 (A), polyisocyanate compound (B) and polycarbonate diol
compound (C) in the coating composition of the invention
are preferably: hydroxyl group-containing resin (A) = 30-
75 mass% and more preferably 40-65 mass%, polyisocyanate
compound (B) = 20-65 mass% and more preferably 30-55
15 mass% and polycarbonate diol compound (C) = 3-30 mass%,
more preferably 5-25 mass% and even more preferably 10-20
mass%, as the nonvolatile components based on 100 parts
by mass as the total solid content of components (A), (B)
and (C).

20 Other components

The paint is a coating composition comprising the
aforementioned hydroxyl group-containing resin (A),
polyisocyanate compound (B) and polycarbonate diol
compound (C) as essential components, usually also
25 containing an organic solvent, and if necessary further
containing paint additives commonly used in the field of
paints, such as curing catalysts, pigments, pigment
dispersants, leveling agents, ultraviolet absorbers,
light stabilizers, plasticizers and the like.

30 As examples of curing catalysts there may be
mentioned organometallic catalysts such as tin octylate,
dibutyltin di(2-ethyl hexanoate), dioctyltin di(2-ethyl
hexanoate), dioctyltin diacetate, dibutyltin dilaurate,
dibutyltin oxide, dioctyltin oxide, lead 2-
35 ethylhexanoate, and tertiary amines.

These compounds may be used as curing catalysts
either alone or in mixtures of two or more. The amount

of curing catalyst used will differ depending on its type, but usually it will be 0-5 parts by mass and preferably about 0.1-4 parts by mass with respect to 100 parts by mass as the total solid content of components (A), (B) and (C).

As examples of pigments there may be mentioned color pigments (D) such as titanium oxide, zinc flower, carbon black, cadmium red, molybdenum red, chromium yellow, chromium oxide, Prussian blue, cobalt blue, azo pigment, phthalocyanine pigment, quinacridone pigment, isoindoline pigment, threne pigments, perylene pigments and the like; body pigments such as talc, clay, kaolin, baryta, barium sulfate, barium carbonate, calcium carbonate, silica, alumina white and the like; and metallic pigments such as aluminum powder, mica powder and titanium oxide-coated mica powder.

These pigments may be used alone or in combinations of two or more. The content of the pigment will differ depending on its type, but usually it will be 0-200 parts by mass and preferably about 1-100 parts by mass with respect to 100 parts by mass as the total solid content of components (A), (B) and (C).

The content of a color pigment will differ depending on its type, but usually it will be 0-150 parts by mass and preferably about 1-100 parts by mass with respect to 100 parts by mass as the total solid content of components (A), (B) and (C).

Conventional known ultraviolet absorbers may also be used, and as examples there may be mentioned ultraviolet absorbers such as benzotriazole-based absorbers, triazine-based absorbers, salicylic acid derivative-based absorbers and benzophenone-based absorbers.

From the standpoint of weather resistance and yellowing resistance, the content of an ultraviolet absorber in the coating composition is usually preferred to be in the range of 0-10 parts by mass, particularly 0.2-5 parts by mass and especially 0.3-2 parts by mass

with respect to 100 parts by mass of the total solid portion of the resin.

Conventional known light stabilizers may also be used, examples of which include hindered amine-based
5 light stabilizers.

From the standpoint of weather resistance and yellowing resistance, the content of a light stabilizer in the coating composition will usually be in the range of 0-10 parts by mass, particularly 0.2-5 parts by mass
10 and especially 0.3-2 parts by mass with respect to 100 parts by mass as the total solid portion of the resin.

When the isocyanate groups of the polyisocyanate compound as component (B) are not blocked in the coating composition of the invention, from the standpoint of
15 storage stability it is preferred to use a two-pack paint separating the hydroxyl group-containing resin (A) and the polycarbonate diol compound (C) from the polyisocyanate compound (B), with both components being mixed just prior to use.

20 Coating method for coating composition

There are no particular restrictions on objects to which the paint may be applied, but as preferred examples there may be mentioned vehicle bodies of automobiles, two-wheeled vehicles, transport containers and the like.
25 The materials forming the vehicle bodies may be steel sheets such as cold-rolled steel sheets, zinc-plated steel sheets, zinc alloy-plated steel sheets, stainless steel sheets, tin-plated steel sheets and the like, metal bases such as aluminum sheets and aluminum alloy sheets,
30 or various plastic materials.

The objects may be metal surfaces of vehicle bodies or metal base materials that have been surface treated by phosphate treatment, chromate treatment, complex oxide treatment or the like. The vehicle body, metal base
35 material or the like may also include a ground coating film and/or intercoat coating film composed of an electrocoated paint or the like.

The coating method is not particularly restricted, and for example, there may be mentioned air spray coating, airless spray coating, rotary atomizing coating, curtain coat coating or the like, which methods allow
5 formation of wet coating films. An electrostatic charge may also be applied if necessary in these coating methods. Particularly preferred among the aforementioned methods is air spray coating. The paint coating coverage is usually preferred to be about 10-50 μm as the cured
10 film thickness.

When carrying out air spray coating, airless spray coating or rotary atomizing coating, the viscosity of the paint is preferably adjusted as appropriate using an
15 organic solvent or other solvent to within a suitable viscosity range for coating, and usually to a viscosity range of about 15-60 seconds at 20°C as measured with a Ford cup No.4 viscometer.

The wet coating film obtained by coating the paint onto the object is cured by heating, which may be
20 accomplished by known heating means with a dry furnace such as, for example, an air heating furnace, electric furnace, infrared ray induction heating furnace or the like. The heating temperature is in the range of 60-180°C and preferably 90-150°C. Although the heating time is not
25 especially restricted, it is preferably in the range of 15-30 minutes.

Because the paint can provide a cured coating film with excellent mar resistance, acid resistance, stain
30 resistance and finished appearances, it can be suitably used as a finishing top clear coat paint. The paint is particularly suitable as an automobile paint.
Multilayer coating film forming method

The multilayer coating film forming method by which the paint is applied as a finishing top clear coat paint
35 may be a method of forming a multilayer coating film by coating at least one colored base coat paint and at least

one clear coat paint in that order on the object, wherein the coating composition of the invention is applied as the uppermost clear coat paint layer.

Specifically, there may be mentioned a two-coat one-bake type multilayer method of forming a coating film in which, for example, a solution-type or aqueous base coat paint is applied onto an object having an electrodeposited paint and/or intercoat paint layer, and the paint of the invention is applied as a clear coat paint onto the uncured base coat coating film (which is uncured but if necessary is preheated at 40-90°C for about 3-30 minutes to promote volatilization of the solvent in the base coat paint), after which the base coat and clear coat are cured together.

The paint of the invention is preferably used as the top clear coat paint for finish coating in a three-coat two-bake system or a three-coat one-bake system.

The base coat paint used may be a thermosetting base coat paint that is known in the prior art, and as a specific example, there may be used a paint comprising a base resin such as an acrylic resin, polyester resin, alkyd resin or urethane resin with a curing agent such as an amino resin, polyisocyanate compound, block polyisocyanate compound or the like, as appropriate for combination with the reactive functional groups in the base resin.

The base coat paint is preferably a high-solid type with minimal use of organic solvents from the standpoint of the environment and resource usage, while a water-based paint or powder coating may also be used.

When using two or more clear coats in a multilayer method of forming a coating film, the clear coat paint used in addition to the paint of the invention may be any ordinary thermosetting clear coat paint known in the prior art.

The present invention will now be explained in greater detail using examples and comparative examples.

However, it is to be understood that the invention is not limited to these examples. The "parts" and "%" values used throughout are all based on mass, and the coating film thicknesses are all based on the cured coating film.

5 Hydroxyl group-containing resin production examples
Production Examples 1-16

After charging 31 parts of ethoxyethyl propionate into a four-necked flask equipped with a stirrer, thermometer, condenser tube and nitrogen gas inlet, the
10 temperature was raised to 155°C under a nitrogen gas stream. When the temperature reached 155°C, the nitrogen gas stream was interrupted and a monomer mixture having a composition comprising the monomers and polymerization
15 initiators listed in Table 1 below was added dropwise over a period of 4 hours. After then maturing the mixture for 2 hours at 155°C while blowing in nitrogen gas, it was cooled to 100°C and diluted with 32.5 parts of
butyl acetate (7.5 parts in Production Example 12) to obtain a paint resin with a solid content of 60%. The
20 solid concentrations by weight (%) and the resin properties of the obtained hydroxyl group-containing resins are shown in Table 1.

The glass transition temperature (°C) values listed in Table 1 were calculated by the following formulas.

25
$$1/T_g (K) = (W_1/T_1) + (W_2/T_2) + \dots$$

$$T_g(°C) = T_g(K) - 273$$

In these formulas, W1, W2, ... represent the mass fractions of the monomers used for copolymerization, and T1, T2, ... represent the Tg (K) for homopolymers of each
30 of the monomers. T1, T2, ... are the values listed in Polymer Handbook (Second Edition, J. Brandup, E.H. Immergut, ed.).

The glass transition temperature of the hydroxyl group-containing resin of Production Example 12 is the
35 value measured using a DSC220U (differential scanning calorimeter) by Seiko Instruments, Inc. The measurement

was conducted by weighing out 50 mg of sample into a special sample dish and drying it at 130°C for 3 hours, and then raising the temperature from -50°C to 150°C at a speed of 10°C/min in an inert gas, and reading out the temperature at the point of inflection of the obtained heat change curve.

The macromonomer (1) solution in the table was obtained by the following production process.

Production of macromonomer (1) solution

After charging 58.7 parts of butyl acetate and 32 parts of isophorone diisocyanate into a four-neck flask equipped with a stirrer, thermometer, condenser tube and oxygen gas inlet, the mixture was kept heated at 80°C, and then 85 parts of PLACCEL FM3X (solution of ϵ -caprolactone-modified hydroxyethyl methacrylate (reaction product obtained by ring-opening polymerization addition reaction of 3 moles of ϵ -caprolactone with 1 mole of hydroxyethyl methacrylate), solid content: 80%, trade name of Daicel Chemical Industries, Ltd.) and 24.3 parts of butyl acetate were slowly added while blowing in oxygen gas. The mixture was then reacted for 3 hours to obtain addition product (A) solution.

In a separate four-neck flask equipped with a stirrer, thermometer, condenser tube and oxygen gas inlet there were charged 58.5 parts of butyl acetate and 58.5 parts of FLEXORES 188 (polyester oligomer having methylolcyclohexyl groups at both ends, trade name of King Industries, US), the mixture was kept heated at 70°C, and then 83 parts of the aforementioned addition product (A) solution was added dropwise while blowing in oxygen and stirring. The mixture was then reacted for 5 hours to obtain macromonomer (1) solution with a solid content of 50%.

Table 1

		Production Example																
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	
Monomer mixture	Styrene	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	
	N-Butyl acrylate	20	20	20	20	20		20	20		20	20	20	20	20	20	20	
	Isobutyl methacrylate	22	39.1	16	22	22		7			18	17		44	11.3	22	22	
	4-Hydroxybutyl acrylate										42							
	2-Ethylhexyl acrylate						42			14								
	Isobornyl acrylate						42			13								
	3-Methacryloxypropyltrimethoxysilane								15	15								
	2-Hydroxyethyl methacrylate	38	20.9	44	38	38	38	38	38	38		28	35	16	48.7	38	38	
	1,4-Cyclohexanedimethanol monoacrylate											15						
	50% Macromonomer (1) solution												50					
	2,2-Di(t-amyloperoxy)butane (*1)	5	5	5	10	0.6	5	5	5	5	5	5	5	5	5	5	11	0.5
	Solid concentration by mass (%)	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60
	Wt-av. molecular weight	10000	10000	10000	2800	38000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	2300	42000
	Hydroxyl value (mgKOH/g)	164	90	190	164	164	164	164	164	164	164	164	164	159	69	210	164	164
	Glass transition temperature (°C)	31.6	31.3	31.3	31.6	31.6	79.6	4.5	21.7	34.2	-21	13.1	5.0	31.2	31.8	31.6	31.6	31.6

(*1) Polymerization initiator

Resin properties

Production of coating composition

Examples 1-18 and Comparative Examples 1-9

The hydroxyl group-containing resins obtained in Production Examples 1-16 above and the starting materials listed in Table 2 below were combined and stirred with a disper mixer in the proportions listed in Table 2 to obtain coating compositions. The proportions of the coating compositions listed in Table 2 are the solid weight ratios for each component.

The notes (*1)-(*12) in Table 2 represent the following, and the viscosities are the values measured using a Brookfield viscometer under conditions of 50°C, 6 rpm.

(*1) N-3300: Hexamethylene diisocyanate, solid content: 100%, NCO content: 21.8%, product of Sumika Bayer Urethane Co., Ltd.

(*2) TAKENATE D160N: hexamethylene diisocyanate and trimethylolpropane adduct, solid content: 75%, NCO content: 12.6%, product of Takeda Pharmaceutical Co., Ltd.

(*3) T-5650J: Polycarbonate diol comprising 1,6-hexanediol and 1,5-pentanediol as diol components, number-average molecular weight: 800, viscosity: 860 mPa·s, hydroxyl value: 140 mgKOH/g, solid content: 100%, product of Asahi Kasei Corp.

(*4) T-4671: Polycarbonate diol comprising 1,6-hexanediol and 1,4-butanediol as diol components, number-average molecular weight: 1000, viscosity: 2400 mPa·s, hydroxyl value: 112 mgKOH/g, solid content: 100%, product of Asahi Kasei Corp.

(*5) PC-M: Polycarbonate diol synthesized using 1,6-hexanediol and 3-methylpentanediol as diol components and diphenyl carbonate as a carbonylating agent, number-average molecular weight: 2000, viscosity: 7000 mPa·s, hydroxyl value: 56 mgKOH/g, solid content: 100%.

(*6) UM-CARB90: Polycarbonate diol comprising 1,6-hexanediol and 1,4-cyclohexanedimethanol as diol

components, number-average molecular weight: 900, viscosity: 7000 mPa·s, hydroxyl value: 124 mgKOH/g, solid content: 100%, product of Ube Industries, Ltd.

(*7) UV1164: Ultraviolet absorber by Ciba-Geigy, K.K.

5 (*8) HALS292: Light stabilizer by Ciba-Geigy, K.K.

(*9) T-4672: Polycarbonate diol comprising 1,6-hexanediol and 1,4-butanediol as diol components, number-average molecular weight: 2000, viscosity: 20,000 mPa·s, hydroxyl value: 112 mgKOH/g, solid content: 100%, product of Asahi
10 Kasei Corp.

(*10) PC-L: Polycarbonate diol synthesized using 1,6-hexanediol and 3-methylpentanediol as diol components and diphenyl carbonate as a carbonylating agent, number-average molecular weight: 380, viscosity: 120 mPa·s,
15 hydroxyl value: 295 mgKOH/g, solid content: 100%.

(*11) PC-H: Polycarbonate diol synthesized using 1,6-hexanediol and 3-methylpentanediol as diol components and diphenyl carbonate as a carbonylating agent, number-average molecular weight: 2800, viscosity: 15,000 mPa·s,
20 hydroxyl value: 40 mgKOH/g, solid content: 100%.

(*12) PC-012: Polycarbonate diol synthesized using 1,6-hexanediol and 1,2-dodecanediol as diol components and diphenyl carbonate as a carbonylating agent, number-average molecular weight: 1000, viscosity: 20,000 mPa·s,
25 hydroxyl value: 112 mgKOH/g, solid content: 100.

The coating compositions obtained in Examples 1-18 and Comparative Examples 1-9 were adjusted to a viscosity of 25 seconds at 20°C using a Ford cup No.4 with addition of butyl acetate.

30 Fabrication of test panel

The viscosity-adjusted coating compositions obtained in Examples 1-18 and Comparative Examples 1-9 were used to prepare test panels in the following manner.

35 A 0.8 mm-thick dull steel sheet chemically treated with zinc phosphate was electrodeposited with ELECRON GT-10 (thermosetting epoxy resin-based cationic electrodeposition paint, trade name of Kansai Paint Co.,

Ltd.) to a film thickness of 20 μm and heated at 170°C for 30 minutes to curing, and then AMYLAC TP-65-2 (polyester/melamine resin-based automotive intercoat paint, trade name of Kansai Paint Co., Ltd.) was air spray coated thereover to a film thickness of 35 μm and heated at 140°C for 30 minutes for curing. The water-based metallic base coat WBC713T#202 (acryl/melamine resin-based automobile top base coat paint, black, product of Kansai Paint Co., Ltd.) was coated on the coating film to a film thickness of 15 μm , allowed to stand at room temperature for 5 minutes and then preheated at 80°C for 10 minutes, after which each of the viscosity-adjusted coating compositions produced in the examples and comparative examples was painted on the uncured coating film to a film thickness of 35 μm , allowed to stand at room temperature for 10 minutes and heated at 140°C for 20 minutes to cure both coating films together to obtain a test panel. Each of the obtained test panels was allowed to stand at ordinary temperature for 7 days and then subjected to the following film performance test.

Performance test method

Mar resistance: An automobile having the test panel attached to the roof using water-resistant tape by Nichiban Co., Ltd. was washed 15 times with a car wash system at 20°C, and then the 20° mirror reflectivity (20° gloss) was measured and compared to the 20° gloss before the test, for evaluation as the gloss retention (%). A higher gloss retention represents more satisfactory mar resistance. The car wash system used was "PO20 FWRC" by Yasui Sangyo Co., Ltd.

Acid resistance: 40% sulfuric acid was added dropwise to 0.4 cc on the coating film of each test panel, after which the sheet was heated for 15 minutes on a hot plate heated to 60°C and washed with water. The

etching thickness (μm) at the sulfuric acid dropping location was measured using a surface roughness tester (SURFCOM 570A surface roughness profile measuring device by Tokyo Seimitsu Co., Ltd.) with a cutoff of 0.8 mm (scanning speed: 0.3 mm/sec, magnification: 5000x) to evaluate the acid resistance. A smaller etching depth represents more satisfactory acid resistance.

Finished appearances (gloss): This was evaluated by measuring the 20° mirror reflectivity (20° gloss) of the test panel.

Stain resistance: Each painted test panel was tested for 600 hours in a sunshine weather meter (accelerated weather resistance tester by Suga Test Instruments, Co., Ltd.), and then a contaminant mixture comprising mud, carbon black, mineral oil and clay was applied onto flannel and lightly rubbed on the painted surface of each test panel. After allowing this to stand for 24 hours in a steady temperature/humidity room at 20°C, 75% RH, the painted surface was washed with flowing water and the degree of staining of the coating film was evaluated based on the following equation for brightness difference (ΔL) of the coated panel. A smaller ΔL value represents more satisfactory stain resistance. ΔL was calculated by the following equation.

$$\Delta L = (\text{L value before stain resistance test}) - (\text{L value after stain resistance test})$$

The L value was measured using a CR-200 (color difference meter by Minolta Camera Co.)

Very good (VG): $\Delta L < 0.2$

Good (G): $0.2 \leq \Delta L < 1$

Fair (F): $1 \leq \Delta L < 2$

Poor (P): $2 \leq \Delta L$

For the contamination test, a 0.8 mm-thick dull steel sheet chemically treated with zinc phosphate was electrodeposited with ELECRON GT-10 (thermosetting epoxy

resin-based cationic electrodeposition paint, trade name
of Kansai Paint Co., Ltd.) to a film thickness of 20 μm
and heated at 170°C for 30 minutes to curing, and then
5 AMYLAC TP-65-2 (polyester/melamine resin-based automobile
intercoat paint, white, trade name of Kansai Paint Co.,
Ltd.) was air spray coated thereover to a film thickness
of 35 μm and heated at 140°C for 30 minutes for curing,
and over this coating film each viscosity-adjusted
10 coating composition produced in the examples and
comparative examples was coated to a film thickness of 35
 μm , allowed to stand at room temperature for 10 minutes
and heated at 140°C for 20 minutes for curing to obtain
test panels, each of which was used for the stain
15 resistance test after standing at ordinary temperature
for 7 days.

The performance test results are shown in Table 2.

Table 2

		Example																							
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18						
Hydroxyl-containing resin	Type (Production Example No.)	1	1	1	1	1	1	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	Amount (parts)	55	48	55	57	55	45	57	62	52	55	55	55	55	55	55	55	55	55	55	55	55	55	55	55
N-3300(*1)		35		35	33	35	35	36	28	38	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35
TAKENATE D-160N (*2)			42																						
T-5650J (*3)		10	10				20	7.5	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
T-4671(*4)				10																					
PC-M (*5)					10																				
UMCARB90(*6)						10																			
UV1164(*7)		2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
HALS292(*8)		2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Test results	Mar resistance	90	95	90	90	83	95	85	83	91	91	85	83	93	85	84	93	94	93	93	85	84	93	94	93
	Acid resistance (µm)	0.4	0.5	0.4	0.4	0.3	0.4	0.4	0.4	0.4	0.4	0.5	0.4	0.3	0.4	0.3	0.2	0.3	0.2	0.3	0.4	0.3	0.2	0.3	0.3
	Stain resistance	G	G	G	G	G	G	G	G	G	G	VG	VG	G	G	VG	G	G	VG	G	G	VG	G	G	VG
	Finished appearances (gloss)	90	90	90	88	90	90	90	90	89	91	90	90	90	90	90	88	90	88	90	90	88	90	88	88

Table 2 (continued)

		Comparative Example								
		1	2	3	4	5	6	7	8	9
Hydroxyl-containing resin	Type (Production Example No.)	1	13	14	15	16	1	1	1	1
	Amount (parts)	64	65	50	55	55	57	51	57	55
N-3300 (*1)		36	25	40	35	35	33	39	33	35
T-5650J (*3)			10	10	10	10				
T-4672 (*9)							10			
PC-L (*10)								10		
PC-H (*11)									10	
PC-012 (*12)										10
UV1164 (*7)		2	2	2	2	2	2	2	2	2
HALS292 (*8)		2	2	2	2	2	2	2	2	2
Test results	Mar resistance	71	70	88	88	89	70	90	75	88
	Acid resistance (μm)	1.0	0.5	0.5	0.7	0.4	0.4	0.9	0.5	0.5
	Stain resistance	G	G	P	F	G	P	G	P	P
	Finished appearances (gloss)	90	89	70	90	79	50	90	50	40

Industrial Applicability

The present invention is industrially useful because it provides a coating composition that can provide coating films with excellent mar resistance, acid resistance, stain resistance and finished appearances.

CLAIMS

1. A coating composition comprising (A) a hydroxyl group-containing resin with a hydroxyl value of 80-200 mgKOH/g and a weight-average molecular weight of 2500-40,000, (B) a polyisocyanate compound, and (C) a polycarbonate diol compound of number-average molecular weight 400-2500 with a viscosity of no greater than 10,000 mPa·s at 50°C, obtained by reacting a C2-10 diol as the diol component with a carbonylating agent.
2. A coating composition according to claim 1, wherein the polycarbonate diol compound (C) employs 1,6-hexanediol as the diol component.
3. A coating composition according to claim 1 or 2, wherein the hydroxyl group-containing resin (A) is a hydroxyl group-containing acrylic resin.
4. A coating composition according to claim 3, wherein the hydroxyl group-containing acrylic resin is a hydroxyl group-containing acrylic resin obtained by copolymerizing a monomer mixture containing a hydroxyl group-containing unsaturated monomer with a C4 or greater hydroxyl group-containing hydrocarbon group.
5. A coating composition according to claim 3, wherein the hydroxyl group-containing acrylic resin is a hydroxyl group-containing acrylic resin obtained by copolymerizing a monomer mixture containing an unsaturated monomer with a C10-20 bridged alicyclic hydrocarbon group and/or an unsaturated monomer with a C3-12 alicyclic hydrocarbon group.
6. A coating composition according to claim 3, wherein the hydroxyl group-containing acrylic resin is a hydroxyl group-containing acrylic resin obtained by copolymerizing a monomer mixture containing an unsaturated monomer with a C8 or greater hydrocarbon group having a branched structure.
7. A coating composition according to claim 3, wherein the hydroxyl group-containing acrylic resin is a hydroxyl group-containing acrylic resin obtained by

copolymerizing a monomer mixture including an alkoxy silane group-containing unsaturated monomer.

8. A coating composition according to claim 3, wherein the hydroxyl group-containing acrylic resin is a hydroxyl group-containing acrylic resin obtained by copolymerizing a monomer mixture including an unsaturated monomer which contains both a cyclohexyl ring and a hydroxyl group.

9. A coating composition according to any one of claims 1 to 8, wherein the polyisocyanate compound (B) is at least one selected from the group consisting of aliphatic diisocyanates and their derivatives.

10. A coating composition according to any one of claims 1 to 9, which further contains (D) a color pigment.

11. A method for forming a multilayer coating film whereby a multilayer coating film is formed by applying at least one colored base coat paint and at least one clear coat paint in that order on an object, wherein a coating composition according to any one of claims 1 to 10 is applied as the uppermost clear coat paint layer.

INTERNATIONAL SEARCH REPORT

International application No

PCT/JP2007/054144

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09D175/04 C08G18/65 C08G18/40 C08G18/44

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)

C09D 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

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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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O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

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INTERNATIONAL SEARCH REPORT

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