

DESCRIPTION

LOW-TEMPERATURE-CURABLE CLEAR COATING COMPOSITION

TECHNICAL FIELD

[0001] The present invention relates to a low-temperature-curable clear coating composition.

BACKGROUND ART

[0002] Generally, the outer plate of a car body is required to prevent the deterioration of a coated film and the generation of lust and have durability so as to maintain the gloss or color of the coated film. Accordingly, the painting process of cars is generally conducted through the electrodeposition coating of a car body which has undergone a pre-treatment process, primer coating for improving adhesiveness and smoothness, and basecoat coating of the car body which has undergone the primer coating for the appearance of the car body. After that, generally, a clearcoat film is coated to protect the color and improve the appearance of the basecoat film, and protect the basecoat film from the outside.

[0003] As the conventional clear paint for cars, a thermosetting coating composition of a resin including a hydroxyl group and an amino resin has been widely used. However, in case of using the conventional thermosetting coating composition, the appearance of parts composed of plastic materials such as bumpers and rearview mirrors may be modified or twisted during curing under high-temperature curing conditions, and the parts are required to be separated to separately perform painting processes, inconveniently. In

addition, there are defects in that the color of the parts of the plastic materials, separated from a car body and separately painted becomes different from the color of the car body itself. Accordingly, a low-temperature-curable clear coating composition which reduces the curing temperature receives attention so as to perform the painting process with respect to one body of the parts of the plastic materials combined with the car body.

[0004] As an alternative, Korean Registration Patent No. 1,655,621 (Patent Document 1) discloses a clear coating composition including two types of acrylic polyol resins, a polyester polyol resin, a reactive silicone additive and an isocyanate curing agent. However, the conventional low-temperature-curable clear coating composition such as the clear coating composition of Patent Document 1 has insufficient mechanical properties of a coated film formed therefrom, and could be applied only for painting for repairing or for parts, and there are limitations in applying for painting a car body.

[0005] Accordingly, research and development on a clear coating composition which could be cured at a low temperature of 120°C or less, could serve a coated film having excellent mechanical properties and could be suitably applied for painting a car body, is required.

DISCLOSURE OF THE INVENTION

TECHNICAL PROBLEM

[0006] The present invention provides a clear coating composition which is curable at a low temperature of 120°C or less and manufacturing a coated film having excellent mechanical properties.

TECHNICAL SOLUTION

[0007] The present invention provides a low-temperature-curable clear coating composition, including a silicone-modified polyester polyol resin, an acrylic polyol resin and an isocyanate resin.

ADVANTAGEOUS EFFECTS

[0008] The clear coating composition according to the present invention is curable at a low temperature of 120°C or less, is capable of saving costs required during a painting process and is economical, and could be coated on one body of a car body and material parts combined therewith, and accordingly, defects concerning different colors of the parts and the car body after painting may be prevented. In addition, since both the car body and the parts could be painted by one time of a painting process, the inconvenience associated with the process and the loss of costs may be removed. Further, a coated film formed from the clear coating composition has excellent mechanical properties such as hardness, adhesiveness, water resistance, acid resistance, scratch resistance and solvent resistance, and may be usefully used for painting a car body.

BEST MODE FOR CARRYING OUT THE INVENTION

[0009] The low-temperature-curable clear coating composition according to the present invention includes a silicone-modified polyester polyol resin, an acrylic polyol resin and an isocyanate resin.

[0010] Silicone-modified polyester polyol resin

[0011] The silicone-modified polyester polyol resin plays the role of providing a composition with the forming properties of a coated film.

[0012] The silicone-modified polyester polyol resin may

include a first repeating unit derived from an organic polysiloxane, a second repeating unit derived from a polyfunctional alcohol and a third repeating unit derived from a polyfunctional carboxylic acid. For example, the silicone-modified polyester polyol resin may be composed of a first repeating unit derived from an organic polysiloxane, a second repeating unit derived from a polyfunctional alcohol and a third repeating unit derived from a polyfunctional carboxylic acid. That is, the silicone-modified polyester polyol resin may be prepared through the reaction of an organic polysiloxane, a polyfunctional alcohol monomer and a polyfunctional carboxylic acid monomer. In another embodiment, the silicone-modified polyester polyol resin may be prepared through the condensation reaction of an organic polysiloxane, a polyfunctional alcohol monomer and a polyfunctional carboxylic acid monomer.

[0013] The organic polysiloxane may include a functional group and a non-functional organic group. For example, the organic polysiloxane may include one or more functional groups selected from the group consisting of silanol and an alkoxy group, and one or more non-functional groups selected from the group consisting of methyl, propyl and phenyl groups. The alkoxy group may include, for example, methoxy, ethoxy and butoxy groups.

[0014] The organic polysiloxane may have a number average molecular weight of 100 to 5,000 g/mol. For example, the organic polysiloxane may have a number average molecular weight of 200 to 5,000 g/mol, 300 to 4,000 g/mol, or 500 to 3,000 g/mol.

[0015] The organic polysiloxane may include DC-3037, DC-3074,

RSN-0217, RSN-0220, RSN-0233, RSN-0255 and RSN-6018 of Dow Corning Co., and SY300, IC836, REN168, SY409, IC232, SY231, IC368, IC678, 601, 603, and 604 among SILRES series of Wacker Co.

[0016] The polyfunctional alcohol monomer may be, for example, one or more selected from the group consisting of ethylene glycol, propylene glycol, trimethylolpropane, trimethylolethane, cyclohexanedimethanol, neopentyl glycol, 2-butyl-2-ethyl-1,3-propanediol, 1,6-hexanediol, diethylene glycol, dipropylene glycol, tripropylene glycol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, triethylolpropane, glycerine and pentaerythritol.

[0017] The polyfunctional carboxylic acid monomer may be, for example, one or more selected from the group consisting of phthalic anhydride, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, succinic anhydride, isophthalic acid, azelaic acid, maleic anhydride and trimellitic anhydride.

[0018] The silicone-modified polyester polyol resin may be prepared through the reaction of 100 parts by weight of an organic polysiloxane, 300 to 800 parts by weight of a polyfunctional alcohol monomer and 300 to 600 parts by weight of a polyfunctional carboxylic acid monomer. For example, the silicone-modified polyester polyol resin may be prepared through the reaction of 100 parts by weight of an organic polysiloxane, 400 to 700 parts by weight, or 500 to 650 parts by weight of a polyfunctional alcohol monomer and 350 to 550 parts by weight, or 400 to 500 parts by weight of a polyfunctional carboxylic acid monomer. In case of preparing

the silicone-modified polyester polyol resin by using the monomers in the aforementioned amount ranges, the improving effects of the appearance characteristics and scratch resistance of a coated film formed from a paint composition including the same may be achieved.

[0019] The silicone-modified polyester polyol resin may have a hydroxyl value of 150 mgKOH/g to 350 mgKOH/g, an acid value of greater than 0 mgKOH/g and 30 mgKOH/g or less, a number average molecular weight of 100 to 10,000 g/mol, and a glass transition temperature of -50°C to 30°C . In another embodiment, the silicone-modified polyester polyol resin may have a hydroxyl value of 150 mgKOH/g to 300 mgKOH/g, or 200 mgKOH/g to 300 mgKOH/g, an acid value of 1 mgKOH/g to 30 mgKOH/g, or 1 mgKOH/g to 20 mgKOH/g, a number average molecular weight of 100 to 5,000 g/mol, or 100 to 2,000 g/mol, and a glass transition temperature of -30°C to 30°C , or greater than 0°C and 20°C or less.

[0020] In case where the hydroxyl value of the silicone-modified polyester polyol resin is in the aforementioned range, improving effects curability may be achieved, in case where the acid value is in the aforementioned range, effects of controlling reactivity and assisting appearance may be achieved, in case where the number average molecular weight is in the aforementioned range, the formation of excellent appearance may be favorable, and in case where the glass transition temperature is in the aforementioned range, effects of satisfying appearance and paint solid volume ratio (SVR) may be achieved.

[0021]

[0022] Acrylic polyol resin

[0023] The acrylic polyol resin plays the role of providing a composition with the forming properties of a coated film.

[0024] The acrylic polyol resin may include a repeating unit derived from an ethylenically unsaturated monomer and a repeating unit derived from an acrylic monomer including a hydroxyl group. That is, the acrylic polyol resin may be prepared through the reaction of an ethylenically unsaturated monomer and an acrylic monomer including a hydroxyl group. For example, the acrylic polyol resin may be prepared through the reaction of an ethylenically unsaturated monomer, an acrylic monomer including a hydroxyl group and a radical polymerization initiator in a solvent. In another embodiment, the acrylic polyol resin may be prepared through the reaction of an ethylenically unsaturated monomer, an acrylic monomer including a hydroxyl group, a non-functional acrylic monomer, a radical polymerization initiator and a molecular weight controlling agent in a solvent.

[0025] The ethylenically unsaturated monomer may be one or more selected from the group consisting of styrene and derivatives thereof, butadiene, C₁₋₁₂alkyl (meth)acryl and C₁₋₁₂alkyl (meth)acrylic acid ester.

[0026] The acrylic monomer including a hydroxyl group may be one or more selected from the group consisting of hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, cardura acrylate, cardura methacrylate, caprolactone acrylate, caprolactone methacrylate, 2,3-dihydroxypropylacryl, 2,3-dihydroxypropyl methacrylate, polypropylene-modified acrylate, polypropylene-modified methacrylate, 4-hydroxymethylcyclohexyl-methyl acrylate, 4-

hydroxymethylcyclo-methyl methacrylate and ethylenically unsaturated beta-hydroxy ester.

[0027] The ethylenically unsaturated beta-hydroxy ester may be prepared through the reaction of an ethylenically unsaturated acid monomer and an epoxy compound. The ethylenically unsaturated acid monomer may be, for example, a monocarboxylic acid such as (meth)acrylic acid. In addition, the epoxy compound is not concerned with radical polymerization, and may include, for example, glycidyl ether and glycidyl ester.

[0028] The non-functional acrylic monomer may include one or more selected from the group consisting of alkyl (meth)acrylate, cycloalkyl (meth)acrylate and bicycloalkyl (meth)acrylate. For example, the non-functional acrylic monomer may be one or more selected from the group consisting of methyl methacrylate, ethyl methacrylate, iso-butyl methacrylate, n-butyl methacrylate, tert-butyl methacrylate, n-hexyl methacrylate, 2-ethylhexyl methacrylate, iso-bornyl methacrylate, cyclohexyl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, iso-butyl acrylate, n-butyl acrylate, tert-butyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, iso-bornyl acrylate and cyclohexyl acrylate.

[0029] The solvent may use commonly used solvents during radical polymerization without specific limitation and may include, for example, an aromatic hydrocarbon-based solvent such as toluene and xylene; a ketone-based solvent such as methyl ethyl ketone, methyl propyl ketone, methyl butyl ketone and ethyl propyl ketone; an ester-based solvent such as methyl acetate, ethyl acetate, n-propyl acetate, n-butyl acetate and ethyl ethoxypropionate; and an alcohol-based

solvent such as n-butanol, propanol and 1-methoxy-2-propanol.

[0030] In addition, the aromatic hydrocarbon-based solvent may include as a commercial product, KOKOSOL #100, KOKOSOL #150, etc.

[0031] The radical polymerization initiator may use any polymerization initiators commonly used during radical polymerization without specific limitation, and may include, for example, one or more selected from the group consisting of 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobisisobutyronitrile, dibenzoyl peroxide, tert-butylperoxy benzoate, di tert-butyl peroxide, tert-butylperoxy-2-ethylhexanoate, tert-butylperoxy acetate, tert-amyl peroxy-2-ethylhexanoate, di tert-amyl peroxide, cumyl hydroperoxide and dicumyl peroxide.

[0032] The molecular weight controlling agent may use common ones used for preparing an acrylic polyol without specific limitation and may include, for example, mercaptans such as n-dodecyl mercaptan, n-decyl mercaptan, and t-dodecyl mercaptan; and alpha methyl styrene dimer.

[0033] The acrylic polyol resin may have a hydroxyl value of 80 mgKOH/g to 200 mgKOH/g, an acid value of greater than 0 mgKOH/g and 30 mgKOH/g or less, a number average molecular weight of 1,000 to 10,000 g/mol, and a glass transition temperature of greater than 0°C and 70°C or less. In another embodiment, the acrylic polyol resin may have a hydroxyl value of 100 mgKOH/g to 200 mgKOH/g, an acid value of 1 mgKOH/g to 25 mgKOH/g, or 5 mgKOH/g to 15 mgKOH/g, a number average molecular weight of 1,500 to 7,000 g/mol, or 2,000 to 5,000 g/mol, and a glass transition temperature of 10°C to 70°C, or 20°C to 60°C.

[0034] In case where the hydroxyl value of the acrylic polyol resin is in the aforementioned range, the curability of a composition including the same may be improved, in case where the acid value is in the aforementioned range, the reactivity of a composition including the same may be controlled and the appearance characteristics of a coated film formed therefrom may be improved, in case where the number average molecular weight is in the aforementioned range, the appearance characteristics and physical properties of a coated film formed may be suitable, and in case where the glass transition temperature is in the aforementioned range, the initial hardness of a coated film formed may be improved.

[0035] The acrylic polyol resin may be included in an amount of 10 to 40 parts by weight based on 10 to 40 parts by weight of the silicone-modified polyester polyol resin. For example, the acrylic polyol resin may be included in an amount of 15 to 35 parts by weight, or 20 to 30 parts by weight based on 10 to 40 parts by weight of the silicone-modified polyester polyol resin. If the amount of the acrylic polyol resin is within the aforementioned range, defects of deteriorating the gloss of a coated film formed from a coating composition including the same, and defects of deteriorating the appearance characteristics and curing density of a coated film may be prevented.

[0036]

[0037] Isocyanate resin

[0038] The isocyanate resin plays the role of forming a coated film by curing a composition through the crosslinking reaction with components in the composition.

[0039] The isocyanate resin may include one or more functional groups selected from the group consisting of an isocyanurate group, a uretdione group, a biuret group, a urethane group, an allophanate group and an iminooxadiazinedione group. That is, the isocyanate resin may be isocyanate including one or more functional groups selected from the group consisting of an isocyanurate group, a uretdione group, a biuret group, a urethane group, an allophanate group and an iminooxadiazinedione group.

[0040] The isocyanate resin may be prepared from an aliphatic or alicyclic isocyanate. For example, the isocyanate resin may be prepared from an aliphatic isocyanate such as 1,6-hexamethylene isocyanate; and an alicyclic isocyanate such as 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl-cyclohexane (isophoron diisocyanate, IPDI), bis-(4-isocyanatocyclohexyl)-methane, 1-isocyanato-1-methyl-4(3)-isocyanatomethyl cyclohexane, 2,4-hexahydrotoluylene diisocyanate and 2,6-hexahydrotoluylene diisocyanate. For example, the isocyanate resin may be prepared from one or more isocyanates selected from the group consisting of 1,6-hexamethylene diisocyanate, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl-cyclohexane and bis-(4-isocyanatocyclohexyl)-methane.

[0041] The isocyanate resin may be included in an amount of 5 to 40 parts by weight based on 10 to 40 parts by weight of the silicone-modified polyester polyol resin. For example, the isocyanate resin may be included in an amount of 10 to 30 parts by weight, or 15 to 25 parts by weight based on 10 to 40 parts by weight of the silicone-modified polyester polyol resin. If the amount of the isocyanate resin is within the

aforementioned range, defects of deteriorating curing density due to the lack of the reactivity of a composition, and defects of deteriorating the physical properties of a coated film due to the generation of unreacted product in a coated film after curing, may be prevented.

[0042]

[0043] Organic solvent

[0044] The coating composition may additionally include an organic solvent. In this case, the organic solvent plays the role of improving the workability of a composition by controlling the viscosity of a coating composition.

[0045] The organic solvent may include one or more selected from the group consisting of aromatic, acetate-based, alcohol-based and propionate-based solvents. For example, the organic solvent may include an aromatic solvent such as toluene and xylene; an acetate-based solvent such as 1-methoxy-2-propyl acetate, methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate; an alcohol-based solvent such as n-butanol, propanol and 1-methoxy-2-propanol; and a propionate-based solvent such as ethyl ethoxypropionate. In addition, the aromatic solvent may include KOKOSOL #100 and KOKOSOL #150, as a commercial product.

[0046] The organic solvent may be included in an amount of 10 to 50 parts by weight based on 10 to 40 parts by weight of the silicone-modified polyester polyol resin. For example, the organic solvent may be included in an amount of 20 to 40 parts by weight, or 23 to 35 parts by weight based on 10 to 40 parts by weight of the silicone-modified polyester polyol resin. If the amount of the organic solvent is within the aforementioned range, effects of excellent workability during

preparing and painting a coating composition, may be achieved.

[0047]

[0048] Additives

[0049] The coating composition may additionally include one or more additives selected from the group consisting of a curing catalyst, a surface modifier, a light stabilizer, a ultraviolet absorbent, a defoaming agent and a leveling agent.

[0050] The additive may be included in an amount of 0.5 to 20 parts by weight based on 100 parts by weight of the silicone-modified polyester polyol resin. For example, the additive may be included in an amount of 0.8 to 15 parts by weight, or 1 to 10 parts by weight based on 100 parts by weight of the silicone-modified polyester polyol resin.

[0051] The curing catalyst plays the role of preventing incomplete curing of a coating composition and improving the mechanical properties of a coated film formed therefrom. In addition, the curing catalyst may be one or more selected from the group consisting of dibutyltin dilaurate, triethylamine, diethylenetriamine, bismuth carboxylate and zirconium chelate.

[0052] The surface modifier plays the role of controlling the surface tension after applying a coating composition and controlling the smoothness of a coated layer, and may use any one commonly used in a coating composition without specific limitation. For example, the surface modifier may be a surfactant, for example, a silicone-based surfactant.

[0053] The light stabilizer plays the role of improving weather resistance. In addition, the light stabilizer may use any one commonly used in a coating composition without specific limitation, for example, a hindered amine-based one.

For example, the hindered amine-based light stabilizer may include 2,4-bis[N-butyl-N-(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidine-4-yl)amino]-6-(2-hydroxyethylamine)-1,3,5-triazine, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate, etc.

[0054] The ultraviolet absorbent plays the role of absorbing ultraviolet rays to prevent the discoloration of a coating composition and preventing the swelling, delamination and gloss loss of a coated film formed from the coating composition. In addition, the ultraviolet absorbent may use any one commonly used in a coating composition without specific limitation, for example, a benzotriazole-based one such as hydroxyphenyl benzotriazole. For example, the ultraviolet absorbent may use Tinuvin 384 of BASF Co. as a commercial product.

[0055] The defoaming agent plays the role of restraining the generation of bubbles during preparing a coating composition and restraining or removing the phenomenon of pin holes and popping induced during forming a coated film. In addition, the defoaming agent may use any one commonly used in a coating composition without specific limitation. For example, the defoaming agent may use BYK-011, BYK-015 and BYK-072 of BYK Co., DF-21 of Air Product Co., agitan 281 of Munzing Co., Foamster-324 of San Nopco Co., etc.

[0056] The leveling agent plays the role of providing a coating composition with smoothness and improving the appearance characteristics of a coated film formed therefrom to restrain the generation of orange peel. In addition, the leveling agent may use any one commonly used in a coating composition without specific limitation.

[0057]

[0058] 2-liquid type coating composition

[0059] The clear coating composition may be a 2-liquid type coating composition including a main part and a curing agent part. Accordingly, the clear coating composition may be used after mixing the main part and the curing agent part before applying. In this case, the main part may include a silicone-modified polyester polyol resin, an acrylic polyol resin and an organic solvent, and the curing agent part may include an isocyanate resin and an organic solvent.

[0060] The clear coating composition may have the solid content of 40 wt% to 70 wt%. For example, the clear coating composition may have the solid content of 41 wt% to 65 wt%, in another embodiment, 42 wt% to 62 wt%. In case where the clear coating composition has the solid content in the aforementioned range, there are advantages in that the coating workability of the composition is suitable.

[0061] The clear coating composition may be cured at 60°C to 120°C. For example, the clear coating composition may be cured at 70°C to 110°C, or 80°C to 110°C. Since the clear coating composition may be cured in the aforementioned temperature range, costs consumed during a coating process may be saved, and it is economical. In addition, a car body and material parts combined therewith may be coated as one body, defects of different colors between the parts and the car body after coating may be prevented. In addition, since all the car body and the parts may be coated at once, the inconvenience of a process and the cost loss may be solved.

[0062] The clear coating composition may have a viscosity of 10 to 40 seconds based on ford cup number 4. For example,

the clear coating composition may have a viscosity of 15 to 35 seconds, or 20 to 35 seconds based on ford cup number 4. In case where the viscosity of the clear coating composition is less than 10 seconds, defects including vertical flow down may arise, and if the viscosity is greater than 40 seconds, the viscosity of the composition is high, and thus, the appearance characteristics of a coated film formed therefrom may be degraded, or a load may be applied to a coater to be a cause of the disorder of the coater.

[0063] The above-described clear coating composition according to the present invention may be cured at a low temperature of 120°C or less and save the cost consumed during a coating process, and it is economical. In addition, a car body and material parts combined therewith may be coated as one body, defects of different colors between the parts and the car body after coating may be prevented. In addition, since all the car body and the parts may be coated at once, the inconvenience of a process and the cost loss may be solved. Further, a coated film formed from the clear coating composition has excellent mechanical properties such as hardness, adhesiveness, water resistance, acid resistance, scratch resistance and solvent resistance and may be usefully used for coating a car body.

[0064]

MODE FOR CARRYING OUT THE INVENTION

[0065] Hereinafter, the present invention will be explained more particularly referring to embodiments. However, the embodiments are only for assisting the understanding of the present invention, and the scope of the present invention is not limited thereto in any sense.

[0066] In the present invention, the functional group value such as the "acid value" and "hydroxyl value" of a resin may be measured by a method well-known in the art, for example, may represent a value measured by a titration method.

[0067] In addition, the "number average molecular weight" of a resin may be measured by a method well-known in the art, for example, may represent a value measured by a gel permeation chromatography (GPC) method.

[0068] In addition, the "glass transition temperature" of a resin may be measured by a method well-known in the art, for example, may represent a value measured by a differential scanning calorimetry (DSC) method.

[0069]

[0070] [Examples]

[0071] Synthetic Example 1. Preparation of silicone-modified polyester polyol resin

[0072] To a four-neck flask provided with a thermometer, a stirring apparatus, a condenser, a packed column and a separation tube, 123 parts by weight of neopentyl glycol, 317 parts by weight of trimethylolpropane, 170 parts by weight of cyclohexanedimethanol, 114 parts by weight of DC-3074 (product of Dow Corning Co.), and 474 parts by weight of hexahydrophthalic anhydride were injected, and the temperature was raised to 230°C, while removing condensed water under a nitrogen atmosphere. Then, at a point where the acid value of a resin prepared reached 20 mgKOH/g, the packed column was removed, and the reaction was continued. Then, at a point where the acid value of a resin prepared reached 7 mgKOH/g, the temperature was reduced to 130°C, and 480 parts by weight of butyl acetate was added for dilution

to prepare a silicone-modified polyester polyol resin-1.

[0073] The silicone-modified polyester polyol resin-1 thus obtained had the physical properties of a number average molecular weight of 928 g/mol, a hydroxyl value of 250 mgKOH/g, an acid value of 10 mgKOH/g, a glass transition temperature of 10°C, the solid content in the total weight of 70 wt%, and a Gardner viscosity of Y-Z.

[0074]

[0075] Synthetic Example 2. Preparation of silicone-modified polyester polyol resin

[0076] To a four-neck flask provided with a thermometer, a stirring apparatus, a condenser, a packed column and a separation tube, 130 parts by weight of neopentyl glycol, 448 parts by weight of trimethylolpropane, 121 parts by weight of DC-3074 (product of Dow Corning Co.), and 502 parts by weight of hexahydrophthalic anhydride were injected, and the temperature was raised to 230°C, while removing condensed water under a nitrogen atmosphere. Then, at a point where the acid value of a resin prepared reached 20 mgKOH/g, the packed column was removed, and the reaction was continued. Then, at a point where the acid value of a resin prepared reached 7 mgKOH/g, the temperature was reduced to 130°C, and 480 parts by weight of butyl acetate was added for dilution to prepare a silicone-modified polyester polyol resin-2.

[0077] The silicone-modified polyester polyol resin-2 thus obtained had the physical properties of a number average molecular weight of 1,150 g/mol, a hydroxyl value of 280 mgKOH/g, an acid value of 10 mgKOH/g, a glass transition temperature of 5°C, the solid content in the total weight of 70 wt%, and a Gardner viscosity of Z1.

[0078]

[0079] Synthetic Example 3. Preparation of silicone-modified polyester polyol resin

[0080] To a four-neck flask provided with a thermometer, a stirring apparatus, a condenser, a packed column and a separation tube, 306 parts by weight of neopentyl glycol, 87 parts by weight of trimethylolpropane, 141 parts by weight of cyclohexanedimethanol, 132 parts by weight of DC-3074 (product of Dow Corning Co.), and 550 parts by weight of hexahydrophthalic anhydride were injected, and the temperature was raised to 230°C, while removing condensed water under a nitrogen atmosphere. Then, at a point where the acid value of a resin prepared reached 20 mgKOH/g, the packed column was removed, and the reaction was continued. Then, at a point where the acid value of a resin prepared reached 7 mgKOH/g, the temperature was reduced to 130°C, and 480 parts by weight of butyl acetate was added for dilution to prepare a silicone-modified polyester polyol resin-3.

[0081] The silicone-modified polyester polyol resin-3 thus obtained had the physical properties of a number average molecular weight of 1,018 g/mol, a hydroxyl value of 133.7 mgKOH/g, an acid value of 35 mgKOH/g, a glass transition temperature of -10°C, the solid content in the total weight of 70 wt%, and a Gardner viscosity of Y-Z.

[0082]

[0083] Synthetic Example 4. Preparation of polyester polyol resin

[0084] To a four-neck flask provided with a thermometer, a stirring apparatus, a condenser, a packed column and a separation tube, 265 parts by weight of neopentyl glycol, 341

parts by weight of trimethylolpropane, and 676 parts by weight of hexahydrophthalic anhydride were injected, and the temperature was raised to 230°C, while removing condensed water under a nitrogen atmosphere. Then, at a point where the acid value of a resin prepared reached 25 mgKOH/g, the packed column was removed, and the reaction was continued. Then, at a point where the acid value of a resin prepared reached 7 mgKOH/g, the temperature was reduced to 130°C, and 400 parts by weight of butyl acetate was added for dilution to prepare a polyester polyol resin.

[0085] The polyester polyol resin thus obtained had the physical properties of a number average molecular weight of 1,400 g/mol, a hydroxyl value of 195 mgKOH/g, an acid value of 10 mgKOH/g, a glass transition temperature of -5°C, the solid content in the total weight of 75 wt%, and a Gardner viscosity of Z.

[0086]

[0087] Synthetic Example 5. Preparation of acrylic polyol resin

[0088] To a four-neck flask provided with a thermometer, a stirring apparatus, a condenser, and a heating apparatus, 155 parts by weight of KOKOSOL #100, 15 parts by weight of ethyl ethoxypropionate, and 148 parts by weight of glycidyl ester (HEXION Co., CADURA E10P) were purchased and injected, and the temperature was raised to 150°C. Then, if the temperature was stabilized to an isothermal temperature, a monomer mixture was added dropwisely for 300 minutes, and the isothermal temperature was maintained for 120 minutes. In this case, the monomer mixture was prepared by mixing 208 parts by weight of styrene, 125 parts by weight of

hydroxyethyl methacrylate, 54 parts by weight of acrylic acid and 20 parts by weight of di-tert-butyl peroxide.

[0089] Then, the reaction product was cooled to 80°C, and 100 parts by weight of butyl acetate and 100 parts by weight of KOKOSOL #100 were added for dilution to prepare an acrylic polyol resin.

[0090] The acrylic polyol resin thus obtained had the physical properties of the solid content in the total weight of 60 wt%, a Gardner viscosity of Z, a hydroxyl value of 150 mgKOH/g, an acid value of 10 mgKOH/g, a glass transition temperature of 40°C, and a number average molecular weight of 2,030 g/mol.

[0091]

[0092] Hereinafter, the manufacturers and product names of the components used in the Comparative Examples and the Examples are as follows.

[0093] - Isocyanate resin (curing agent): aliphatic polyisocyanate (Desmodur N 3300 of Covestro Co.)

[0094] - Curing catalyst: KOKOSOL #100 including 10 wt% of dibutyltin dilaurate (TL-1)

[0095] - Surface modifier: silicone-based surfactant (BYK-331)

[0096] - Light stabilizer: hindered amine-based light stabilizer (Tinuvin 123 of BASF Co.)

[0097] - Ultraviolet absorbent: Tinuvin 384 of BASF Co.

[0098]

[0099] **Examples 1 to 8 and Comparative Examples 1 to 3.**

Preparation of clear coating composition

[00100] Clear coating compositions were prepared by stirring and mixing the components in the compositions described in

Tables 1 and 2 below at 1,500 rpm for 20 minutes.

[00101] [Table 1]

Component (parts by weight)		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
Silicone-modified polyester polyol resin-1		25	-	35	10	40	7	43
Silicone-modified polyester polyol resin-2		-	25	-	-	-	-	-
Silicone-modified polyester polyol resin-3		-	-	-	-	-	-	-
Polyester polyol resin		-	-	-	-	-	-	-
Acrylic polyol resin		25	25	10	40	10	38	12
Isocyanate resin		20	20	25	20	20	25	15
Additive	Curing catalyst	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Surface modifier	0.2	0.2	0.2	0.2	0.2	0.2	0.2
	Light stabilizer	0.6	0.6	0.6	0.6	0.6	0.6	0.6
	Ultraviolet absorbent	1.1	1.1	1.1	1.1	1.1	1.1	1.1
Organic solvent	KOKOSOL #100	14	14	14	14	14	14	14
	KOKOSOL #150	14	14	14	14	14	14	14
Total amount		100	100	100	100	100	100	100

[00102]

[00103] [Table 2]

Component (parts by weight)		Example 8	Comparative Example 1	Comparative Example 2	Comparative Example 3
Silicone-modified polyester polyol resin-1		-	-	44	-
Silicone-modified polyester polyol resin-2		-	-	-	-
Silicone-modified polyester polyol resin-3		25	-		
Polyester polyol resin		-	24	-	-
Acrylic polyol resin		25	25	-	58
Isocyanate resin		20	19	22	18
Additive	Curing catalyst	0.1	0.1	0.1	0.1
	Surface modifier	0.2	0.2	0.2	0.2
	Light stabilizer	0.6	0.6	0.6	0.6
	Ultraviolet absorbent	1.1	1.1	1.1	1.1
Organic solvent	KOKOSOL #100	14	15	16	12
	KOKOSOL #150	14	15	16	10
Total amount		100	100	100	100

[00104]

[00105] Experimental Example: Measurement of physical

properties of coated film formed from coating composition

[00106] A top coat paint (manufacturer: KCC, product name: WT3090) was applied on a specimen and dried to form a top coat film with a thickness of 15 μm . Then, on the top coat film, each of the clear coating compositions of the Examples and Comparative Examples was applied, and cured at 100°C for 25 minutes to form a clear coat film with a thickness of 40 μm . With respect to the specimen, physical properties were measured by the methods below, and the results are shown in Table 3.

[00107] Particularly, the clear coat film was formed by using a handgun spray (nozzle diameter: 1.5 mm, air pressure: kept constant at around 4.5 kgf/cm²) and moving at a speed of 40-50 cm/sec in the horizontal direction while maintaining the distance from a nozzle inlet to a specimen constant to 30 cm.

[00108] (1) Hardness

[00109] The hardness of a clear coat film was measured by a pencil hardness method. Particularly, the maximum hardness which does not damage the clear coat film was measured by using each pencil of 3B, 2B, B, HB, F, H, 2H and 3H (3B, 2B, B, HB, F, H, 2H, 3H: inferior $\Leftrightarrow$ excellent).

[00110] (2) Adhesiveness

[00111] The specimen was heated and stood at room temperature for 24 hours, and the adhesiveness was evaluated by a baduk board method.

[00112] Particularly, by the baduk board method, on the surface of the clear coat film, 100 squares with a length of 2 mm and a width of 2 mm were formed using a knife, and then, the squares were detached using a tape to measure the adhesiveness. In this case, the adhesiveness measured was

represented by M-1 (very excellent) in case where 100% of the 100 squares were attached completely, M-2 (excellent) in case where remaining squares were 70% to less than 100%, M-3 (common) in case of 50% to less than 70%, M-4 (poor) in case of 30% to less than 50%, and M-5 (very poor) in case of less than 30%.

[00113] In addition, the heat treatment was performed by heating at 150°C for 20 minutes and standing at room temperature for 20 minutes, and this cycle was repeated total three times.

[00114] (3) Water resistance

[00115] The specimen was immersed in a constant-temperature water bath at 40°C for 240 hours and stood at room temperature for 1 hour, and a delamination test was performed by the same method as the baduk-board method of item (2). Also, the same evaluation standard was applied.

[00116] (4) Acid resistance

[00117] On the surface of the coated film of the specimen, 0.2 ml of 0.1 N sulfuric acid was dropped and then, treated in a pre-heated oven at 40°C or more for 150 minutes. In this case, the occurrence of etching, stain or swelling at the portion where the sulfuric acid was dropped on the specimen was observed, and the highest temperature not generating damage on the specimen was judged as the acid resistance temperature.

[00118] (5) Scratch resistance

[00119] 20° gloss of the specimen was measured (initial gloss measurement), the surface of the specimen was treated back and forth 10 times using a washing-resistance tester (product of Amtec Kistler Co.), and then, 20° gloss was measured.

After that, the gloss retention ratio was calculated using Mathematical Equation 1 below using the initial gloss and the gloss after the surface treatment.

[00120] [Mathematical Equation 1]

[00121] Gloss retention ratio = gloss after surface treatment/initial gloss x 100

[00122] (6) Solvent resistance

[00123] On the coated film of the specimen, a cotton swab moistened with xylene was put, the specimen was scratched four times with a force of 2 Kg every one minute, and the time at which the surface of a coated film underneath was appeared, was recorded.

[00124]

[00125] [Table 3]

Item	Solid content in total weight	Hardness	Adhesiveness	Water resistance	Acid resistance	Initial gloss	Scratch resistance (gloss retention ratio)	Solvent resistance
Example 1	52.6 wt%	F	M-1	M-1	45°C	89%	65%	10 min
Example 2	52.4 wt%	F	M-1	M-1	43°C	89%	65%	10 min
Example 3	56 wt%	F	M-1	M-1	44°C	92%	64%	10 min
Example 4	51 wt%	HB	M-1	M-1	43°C	89%	63%	10 min
Example 5	61 wt%	HB	M-1	M-1	43°C	89%	62%	10 min
Example 6	42 wt%	HB	M-1	M-2	40°C	85%	60%	8 min
Example 7	54 wt%	HB	M-1	M-2	41°C	84%	61%	7 min
Example 8	45 wt%	B	M-2	M-2	38°C	84%	61%	8 min
Comparative Example 1	38 wt%	2B	M-2	M-3	38°C	84%	52%	6 min
Comparative Example 2	52.7 wt%	B	M-5	M-2	36°C	85%	54%	5 min
Comparat	39 wt%	3B	M-3	M-3	37°C	85%	53%	5 min

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[00126]

[00127] As shown in Table 3, the coated films formed from the clear coating compositions of Examples 1 to 8 showed excellent mechanical properties including adhesiveness, water resistance, acid resistance, scratch resistance and solvent resistance.

[00128] On the contrary, a coated film formed from the clear coating composition of Comparative Example 1, including the polyester polyol resin showed insufficient water resistance and scratch resistance, and a coated film formed from the clear coating composition of Comparative Example 2, not including the acrylic polyol resin showed insufficient adhesiveness and scratch resistance. In addition, a coated film formed from the clear coating composition of Comparative Example 3, not including the silicone-modified polyester polyol resin showed insufficient mechanical properties including adhesiveness, water resistance and scratch resistance.

[00129]

[00130] As described above, the clear coating composition according to the present invention is curable at a low temperature of 120°C or less, and may save costs consumed during a coating process and be economic. In addition, a car body and material parts combined therewith may be coated as one body, and defects of different colors of the parts and the car body after coating may be prevented. In addition, the coated film formed from the clear composition has excellent physical properties such as hardness, adhesiveness,

water resistance, acid resistance, scratch resistance and solvent resistance, and may be usefully used for coating a car body.

CLAIMS

1. A low-temperature-curable clear coating composition, comprising a silicone-modified polyester polyol resin, an acrylic polyol resin and an isocyanate resin,

wherein the silicone-modified polyester polyol resin has a hydroxyl value of 200 mgKOH/g to 300 mgKOH/g, an acid value of 1 mgKOH/g to 20 mgKOH/g, a number average molecular weight of 100 to 2,000 g/mol, and a glass transition temperature of greater than 0 °C and 20°C or less.

2. The low-temperature-curable clear coating composition according to claim 1, wherein the silicone-modified polyester polyol resin comprises a first repeating unit derived from an organic polysiloxane, a second repeating unit derived from a polyfunctional alcohol and a third repeating unit derived from a polyfunctional carboxylic acid.

3. The low-temperature-curable clear coating composition according to claim 1, wherein the acrylic polyol resin has a hydroxyl value of 80 mgKOH/g to 200 mgKOH/g, an acid value of greater than 0 mgKOH/g and 30 mgKOH/g or less, a number average molecular weight of 1,000 to 10,000 g/mol, and a glass transition temperature of greater than 0°C and 70°C or less.

4. The low-temperature-curable clear coating composition according to claim 1, wherein the acrylic polyol resin comprises a repeating unit derived from an ethylenically unsaturated monomer and a repeating unit

derived from an acrylic monomer including a hydroxyl group.

5. The low-temperature-curable clear coating composition according to claim 1, wherein the clear coating composition comprises 10 to 40 parts by weight of the silicone-modified polyester polyol resin, 10 to 40 parts by weight of the acrylic polyol resin, and 5 to 40 parts by weight of the isocyanate resin.

6. The low-temperature-curable clear coating composition according to claim 1, wherein the clear coating composition is cured at 60°C to 120°C.