

SPECIFICATION

TITLE OF THE INVENTION: POWDER COATING COMPOSITION AND METHOD FOR PRODUCING THE SAME

5 TECHNICAL FIELD

[0001] This invention relates to a powder coating composition and a method for producing the powder coating composition, and more particularly to a powder coating composition which is capable of forming a coat comprising a fluorine coating layer and a polyester coating layer.
10 Moreover, such a powder coating composition may be referred to as a layer separation type powder coating composition.

BACKGROUND ART

[0002] Recently, global environment concerns such as global warming, ozone layer destruction, acid rain, etc. have largely been dealt with, and
15 measures against environmental pollution have been internationally publicized. Various regulations, therefore, have been implemented from the viewpoint of environmental conservation. Among them, the release of organic solvents (particularly, volatile organic compounds VOCs) into the atmosphere is a critical problem. In various industries, a movement
20 toward no organic solvent (particularly, no VOC) becomes more active along with a shift to tighter regulation on VOC. In the coating material industry, an eco-friendly coating material which uses no VOC, makes exhaust and wastewater treatments unnecessary and makes recovery and recycling possible is required as a possible alternative to a conventional
25 coating material of an organic solvent type. There are increasing expectations for a powder coating material.

[0003] An acrylic resin-based, polyester resin-based or epoxy resin-based powder coating material is mainly used as a powder coating material. The epoxy resin-based powder coating material, however, is
30 disadvantageous in that it is poor in weather resistance.

[0004] A powder coating material which is capable of forming a multi-layer coat composed of an acrylic resin-based powder coat as an upper layer and an epoxy resin-based powder coat as a lower layer by coating with a mixture of a thermosetting acrylic resin-based powder
5 coating material and a thermosetting epoxy resin-based powder coating material, heating and curing the mixture has been disclosed as a powder coating material improving such a disadvantage (for example, see Patent Documents 1-3).

[0005] Meanwhile, a thermosetting fluororesin-based powder coating
10 material, which uses a fluororesin having better weather resistance than an acrylic resin or an epoxy resin, has been developed from the viewpoint of improving weather resistance (for example, see Patent Document 4). In the powder coating material which uses only a fluororesin as a resin, however, an expensive fluororesin is required in large amounts, and hence
15 the cost tends to be higher.

CONVENTIONAL ART DOCUMENT LIST

PATENT DOCUMENT

- [0006] Patent Document 1: Japanese Patent Application Publication No. S53-140336
20 Patent Document 2: Japanese Patent Application Publication No. S54-105135
Patent Document 3: Japanese Patent Application Publication No. 2001-259520
Patent Document 4: Japanese Patent Application Publication
25 No. 2008-266361

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007] It is, therefore, an object of the invention to provide a layer separation type powder coating composition which has good weather
30 resistance and reduces production cost. It is also another objection of

the invention to provide a method for producing such a powder coating composition.

MEANS OF SOLVING THE PROBLEMS

[0008] The inventors have made various studies in order to achieve
5 the above objects and discovered that the use of a powder coating composition comprising a fluoro-resin with excellent weather resistance, a low-cost polyester resin and a specified curing agent can form a high weather-resistant coat comprising a fluorine coating layer and a polyester coating layer with low cost and reduced processes, and as a result, the
10 invention has been accomplished.

[0009] That is, the powder coating composition according to the invention is characterized by being capable of forming a coat comprising a fluorine coating layer and a polyester coating layer, the powder coating composition comprising a fluoro-resin containing a hydroxyl group or a
15 carboxyl group, a polyester resin containing a hydroxyl group or a carboxyl group and a curing agent selected from the group consisting of β -hydroxyalkylamide, triglycidyl isocyanurate and an isocyanate compound.

[0010] It is preferable that the powder coating composition according
20 to the invention further comprises an epoxy resin.

[0011] It is preferable that the powder coating composition according to the invention further comprises a luster pigment.

[0012] In a preferable embodiment of the powder coating composition according to the invention, the polyester resin is a hydroxyl
25 group-containing polyester resin which has a number average molecular weight of not more than 5000 and a weight average molecular weight of 10000-20000.

[0013] In another preferable embodiment of the powder coating composition according to the invention, the polyester resin has a melt
30 viscosity of not more than 3.5 Pa·s (190°C) and, in an Arrhenius plot on

the basis of melt viscosity (Pa·s) measured under conditions of a measurement start temperature of 200°C and a temperature dropping rate of 10°C/minute, has a gradient of not less than 15000 in a range of 100-120°C.

5 **[0014]** In another preferable embodiment of the powder coating composition according to the invention, the fluororesin is a hydroxyl group-containing fluororesin.

[0015] In another preferable embodiment of the powder coating composition according to the invention, a ratio (A/B) by mass of the
10 fluororesin (A) to the polyester resin (B) is 50/50 to 10/90.

[0016] In another preferable embodiment of the powder coating composition according to the invention, a difference in solubility parameter (SP value) between the fluororesin and the polyester resin is 0.6-0.9.

15 **[0017]** Also, the method for producing the powder coating composition according to the invention is characterized in that it comprises melt-kneading a mixture containing the fluororesin, the polyester resin and the curing agent at 100-160°C, cooling and then pulverizing the mixture to prepare a powder coating composition.

20 **EFFECTS OF THE INVENTION**

[0018] According to the invention, the use of a fluororesin with excellent weather resistance, a low-cost polyester resin and the specified curing agent can provide a layer separation type powder coating composition which is capable of forming a high weather-resistant coat
25 comprising a fluorine coating layer and a polyester coating layer with low cost and reduced processes. The invention can also provide a method for producing such a powder coating composition.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019]

30 **[FIG. 1]** It is a mapping image of fluorine atoms present in the cross

section of a coat.

MODE FOR CARRYING OUT THE INVENTION

[0020] <Powder coating composition>

The powder coating composition according to the invention
5 comprises a fluoro-resin containing a hydroxyl group or a carboxyl group,
a polyester resin containing a hydroxyl group or a carboxyl group and a
curing agent selected from the group consisting of β -hydroxyalkylamide,
triglycidyl isocyanurate and an isocyanate compound, and it is capable of
10 forming a coat comprising a fluorine coating layer and a polyester coating
layer. The powder coating composition according to the invention can
also form a coat with excellent weather resistance while suppressing the
production cost, because an inexpensive polyester resin is used in
addition to a fluoro-resin with excellent weather resistance. When a
15 substrate is coated with the powder coating composition according to the
invention, two coating layers are formed by one coating, so that some
manufacturing processes for the coat can be omitted. Moreover, the
fluorine coating layer refers to a coating layer which is formed based on a
fluoro-resin, and the polyester coating layer refers to a coating layer which
is formed based on a polyester resin.

20 [0021] <Fluoro-resin>

In the powder coating composition according to the invention,
the fluoro-resin is required to be a solid resin at ordinary temperatures,
and the softening point is preferably 50-150°C. The fluoro-resin forms a
fluorine coating layer, which imparts weather resistance to the coat. The
25 ordinary temperature is a temperature of 20°C $\pm$ 15°C (5-35°C) as
specified in JIS Z 8703.

[0022] The fluoro-resin needs to have a reaction site which reacts with
a curing agent, etc., and it contains a hydroxyl group or a carboxylic
group. Thus, the fluoro-resin can be produced, for example, by
30 copolymerizing a fluorine-containing monomer and a monomer

containing a specified reactive group.

[0023] The fluorine-containing monomer includes, for example, vinyl fluoride, vinylidene fluoride, trifluoroethylene, tetrafluoroethylene, bromotrifluoroethylene, chlorotrifluoroethylene, pentafluoropropylene, 5 hexafluoropropylene, (per)fluoroalkyl trifluorovinyl ether [in which the number of carbons of the (per)fluoroalkyl group is 1-18], and so on.

[0024] While, the monomer containing the specified reactive group is a polymerizable monomer containing a hydroxyl group or a carboxyl group as a group to react with a curing agent, etc. (reactive group).

10 [0025] The hydroxyl group-containing polymerizable monomer specifically includes, for example, allyl alcohol; hydroxyalkyl vinyl ethers such as 2-hydroxyethyl vinyl ether, 3-hydroxypropyl vinyl ether, 4-hydroxybutyl vinyl ether, 4-hydroxycyclohexyl vinyl ether, etc.; hydroxyalkyl allyl ethers such as 2-hydroxyethyl allyl ether, 15 3-hydroxypropyl allyl ether, 4-hydroxybutyl allyl ether, 4-hydroxycyclohexyl allyl ether, etc.; hydroxyalkyl (meth)acrylates such as 2-hydroxyethyl (meth)acrylate, etc.; esters of hydroxyalkylcarboxylic acid and vinyl alcohol such as vinyl hydroxyacetate, vinyl hydroxyisobutyrate, vinyl hydroxypropionate, vinyl hydroxybutyrate, 20 vinyl hydroxyvalerate, vinyl hydroxycyclohexylcarboxylate, etc.; hydroxyalkyl allyl esters such as hydroxyethyl allyl ester, hydroxypropyl allyl ester, hydroxybutyl allyl ester, hydroxyisobutyl allyl ester, etc.

[0026] The carboxyl group-containing polymerizable monomer includes (meth)acrylic acid, carboxyalkyl allyl ester, etc.

25 [0027] Among these reactive group-containing monomers, the hydroxyl group-containing polymerizable monomer is preferable from the viewpoint of the stability of the resin or control of melt viscosity, etc. In other words, the fluororesin is preferably a hydroxyl group-containing fluororesin.

30 [0028] The polymerization for the fluororesin may employ a

polymerizable monomer other than the fluorine-containing monomer and the monomer containing the specified reactive group. Such a polymerizable monomer includes vinyl ethers, olefins, allyl ethers, vinyl esters, allyl esters, (meth)acrylates, amide (meth)acrylates, cyano group-containing monomers, dienes, crotonates, etc.

[0029] The specific example of the polymerizable monomer other than the fluorine-containing monomer and the monomer containing the specified reactive group includes, for example, alkyl vinyl ethers such as methyl vinyl ether, ethyl vinyl ether, butyl vinyl ether, isobutyl vinyl ether, cyclohexyl vinyl ether, chloroethyl vinyl ether, etc.; olefins such as ethylene, propylene, 1-butene, isobutylene, cyclohexene, vinyl chloride, vinylidene chloride, etc.; styrene-based monomers such as styrene, α -methylstyrene, etc.; alkyl allyl ethers such as methyl allyl ether, ethyl allyl ether, butyl allyl ether, cyclohexyl allyl ether, etc.; vinyl esters of carboxylic acid (preferably, fatty acid) such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, vinyl valerate, vinyl hexanoate, vinyl octanoate, vinyl versatate, etc.; allyl esters of carboxylic acid (preferably, fatty acid) such as allyl propionate, allyl acetate, etc.; (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, cyclohexyl (meth)acrylate, etc.; amide (meth)acrylates such as amide (meth)acrylate, etc.; cyano group-containing monomers such as acrylonitrile, 2,4-dicyanobutene-1, etc.; dienes such as isoprene, butadiene, etc.; crotonates such as 2-hydroxyethyl crotonate, 4-hydroxybutyl crotonate, etc., and so on.

[0030] The polymerization for the fluororesin may employ a polymerizable monomer having a reactive group other than hydroxyl group and carboxyl group. Such a reactive group includes, for example, functional groups such as amide group, amino group, nitrile group, glycidyl group, isocyanate group, etc.

[0031] Specifically, the amino group-containing polymerizable

monomer includes aminoalkyl vinyl ethers and aminoalkyl allyl ethers,
the amide group-containing polymerizable monomer includes
(meth)acrylamide, N-methyl(meth)acrylamide, etc., the nitrile
group-containing polymerizable monomer includes (meth)acrylonitrile,
5 etc., the glycidyl group-containing polymerizable monomer includes
glycidyl allyl ether, glycidyl (meth)acrylate, etc., and the isocyanate
group-containing polymerizable monomer includes vinyl isocyanate,
isocyanatoethyl acrylate, etc.

[0032] In the fluororesin, the content of fluorine is preferably 5-80%
10 by mass, more preferably 10-70% by mass. When the content of fluorine
in the fluororesin is not less than 5% by mass, sufficient weather
resistance can be given to a coat obtained from the powder coating
composition according to the invention. Moreover, when the content of
fluorine in the fluororesin is not more than 80% by mass, sufficient
15 chemical resistance can also be given to the coat. When the fluororesin
is a hydroxyl group-containing fluororesin, the hydroxyl value of the
fluororesin is preferably not more than 100 mgKOH/g from the viewpoint
of keeping the flexibility of the coat, while it is preferably not less than
10 mgKOH/g from the viewpoint of imparting sufficient impact resistance
20 to the coat. In particular, the hydroxyl value of the fluororesin is
preferably 30-70 mgKOH/g.

[0033] <Polyester resin>

In the powder coating composition according to the invention,
the polyester resin can be produced by reacting a carboxylic acid
25 component and a polyhydric alcohol component through a known method.
The polyester resin needs to have a reaction site which reacts with a
curing agent, etc., and hence it contains a hydroxyl group or a carboxylic
group. The polyester resin is required to be a solid resin at ordinary
temperatures, and the softening point is preferably 10-150°C. The
30 polyester resin form a polyester coating layer which constitutes a part of a

coat. Accordingly, the appearance and processability of the coat can be improved and moreover the production cost can be reduced, as compared with a coat composed only of a fluorine coating layer.

[0034] The carboxylic acid component usable in the production of the polyester resin includes, for example, polyvalent carboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid, naphthalene dicarboxylic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, 1,9-nonanedicarboxylic acid, 1,10-decanedicarboxylic acid, 1,12-dodecanedicarboxylic acid, 1,2-octadecanedicarboxylic acid, maleic acid, fumaric acid, cyclohexane dicarboxylic acid, hexahydrophthalic acid, tetrahydrophthalic acid, trimellitic acid, pyromellitic acid, etc., and lower alkyl esters and acid anhydrides of these polyvalent carboxylic acids; and hydroxycarboxylic acids such as malic acid, tartaric acid, 1,2-hydroxystearic acid, paraoxybenzoic acid, etc., and so on.

[0035] The polyhydric alcohol component usable in the production of the polyester resin includes, for example, ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,9-nonanediol, 1,10-decanediol, neopentyl glycol, spiroglycol, 1,10-decanediol, 1,4-cyclohexanedimethanol, trimethylolethane, trimethylolpropane, glycerin, pentaerythritol, etc.

[0036] The polyester resin can be produced using the carboxylic acid component and the polyhydric alcohol component as a raw material, as described above, according to a usual method known in the production of a polyester resin for a powder coating composition. For example, the polyester resin can be produced by using a suitable combination of the various raw materials in a suitable compounding ratio to carry out an esterification or transesterification reaction at 200-280°C according to a conventional method, and thereafter carrying out a polycondensation

reaction using a catalyst at 230-290°C under a reduced pressure, and then possibly a depolymerization reaction with a polyhydric alcohol.

[0037] The polyester resin may have a reactive group other than hydroxyl group and carboxyl group. Such a reactive group includes, for example, functional groups such as amide group, amino group, nitrile group, glycidyl group, isocyanate group, etc.

[0038] The polyester resin is preferably a hydroxyl group-containing polyester resin from the viewpoint of cross-linking reaction or control of coat properties. The polyester resin preferably has a number average molecular weight of not more than 5000 and a weight average molecular weight of 10000-20000 from the viewpoint of control of melt viscosity. The number average molecular weight and weight average molecule weight can be calculated through a gel permeation chromatography (GPC) using polystyrene as a standard substance.

[0039] When the polyester resin is a hydroxyl group-containing polyester resin, the hydroxyl value of the polyester resin is preferably 20-100 mgKOH/g, more preferably 30-80 mgKOH/g. When the hydroxyl value of the polyester resin is less than 20 mgKOH/g, it is hard to obtain enough mechanical properties and solvent resistance for the coat, while when it exceeds 100 mgKOH/g, the amount of a curing agent (for example, isocyanate compound) which adapts to the hydroxyl value is necessary, and the cost is increased. Also, the polyester resin preferably has an acid value of 20-80 mgKOH/g, more preferably 30-80 mgKOH/g. When the acid value of the polyester resin is less than 20 mgKOH/g, it is hard to obtain enough mechanical properties and solvent resistance for the coat, while when it exceeds 100 mgKOH/g, the amount of a curing agent (for example, β -hydroxyalkylamide and triglycidyl isocyanurate) which adapts to the acid value is necessary, and the cost is increased.

[0040] The polyester resin preferably has a melt viscosity of not more than 3.5 Pa·s (190°C). When the melt viscosity of the polyester resin

exceeds 3.5 Pa·s (190°C), it is hard for the layer separation of the coat to take place. In an Arrhenius plot on the basis of melt viscosity (Pa·s) measured under conditions of a measurement start temperature of 200°C and a temperature dropping rate of 10°C/minute, the polyester resin preferably has a gradient of not less than 15000 in a range of 100-120°C. The melt viscosity is measured with a rheometer such as Rheometer ARES made by TA Instruments. Conditions other than measurement start temperature and temperature dropping rate are a parallel plate of 40 mm in diameter, a gap width of 1.0 mm, a frequency of 9.42 rad/s, a strain of 1.0%. The gradient of a line in 100-120°C can be calculated by plotting the measurement results of the melt viscosity on a graph in which the lateral axis is the reciprocal $1/T$ of temperature T (K) and the vertical axis is the logarithm $\ln V$ of melt viscosity V (Pa·s) to create an Arrhenius plot. When the gradient of the line is not less than 15000, it is preferable because the layer separation of the coat is easily formed. More preferably, the gradient is 16000-20000.

[0041] <Epoxy resin>

Preferably, the powder coating composition according to the invention further comprises an epoxy resin in order to improve the adhesion to a substrate.

[0042] In the powder coating composition according to the invention, the epoxy resin is required to be a solid resin at ordinary temperatures, and the softening point is preferably 50-150°C. The epoxy resin is not particularly limited, but an epoxy resin can be used which is conventionally used in the production of an epoxy resin-based powder coating composition.

[0043] The epoxy resin specifically includes, for example, bisphenol A-type diglycidyl ether resin, bisphenol F-type diglycidyl ether resin, amino glycidyl ether resin, bisphenol AD-type diglycidyl ether resin, bisphenol Z-type diglycidyl ether resin, o-cresol novolac epoxy resin,

phenolic novolac epoxy resin, biphenol glycidyl ether resin, cyclopentadiene-skeleton epoxy resin, naphthalene-skeleton epoxy resin, GMA acrylic resin, etc., and a resin in which a substituent group other than the epoxy group of these resins is replaced by other substituent group, for example, a resin obtained through a modification reaction such as a modification reaction with a carboxyl group-terminated polybutadiene-acrylonitrile (CTBN) or esterification, etc., and so on. The epoxy resin preferably has an epoxy equivalent of 300-1200, particularly preferably 400-1000.

10 **[0044]** <Curing agent>

 In the powder coating composition according to the invention, the curing agent is required to be a curing agent selected from the group consisting of β -hydroxyalkylamide, triglycidyl isocyanurate and an isocyanate compound. It can react with a fluoro-resin containing a hydroxyl group or a carboxyl group, a polyester resin containing a hydroxyl group or a carboxyl group, and an epoxy resin to form a cross-linking bond.

[0045] << β -hydroxyalkylamide>>

 When the resin used in the powder coating composition according to the invention has a carboxyl group, it is preferable that β -hydroxyalkylamide is used as a curing agent. The β -hydroxyalkylamide which has not less than two functional groups in one molecule is particularly preferable from the viewpoint of low temperature curability or the water resistance of a coat obtained by coating. N,N-di(β -hydroxyethyl)acetamide, bis(β -hydroxyethyl)adipamide, bis(β -hydroxypropyl)adipamide, bis[N,N-di(β -hydroxyethyl)]adipamide, bis[N,N-di(β -hydroxypropyl)]adipamide are particularly preferable as β -hydroxyalkylamide. β -hydroxyalkylamide preferably has 0.5-1.5 equivalents of a hydroxylamide group based on a carboxyl group of the

resin.

[0046] <<Triglycidyl isocyanurate>>

When the resin used in the powder coating composition according to the invention has a carboxyl group, it is preferable that
5 triglycidyl isocyanurate (TGIC) is used as a curing agent. The triglycidyl isocyanurate includes, for example, Araldite (registered trademark) PT 710, Araldite (registered trademark) PT 810, Araldite (registered trademark) PT 910, Araldite (registered trademark) PT 912 (all products are made by Huntsman Corporation), etc. as a trade name.

10 **[0047]** <<Isocyanate compound>>

From the viewpoint of coat properties such as the hardness of the coat or resistance to hydrolysis, etc., the powder coating composition according to the invention may also be compounded with an isocyanate compound as a curing agent. The isocyanate compound is more
15 preferably a blocked isocyanate compound. Preferably, the isocyanate compound is solid at ordinary temperatures.

[0048] The blocked isocyanate compound is easy to produce, because it can be produced, for example, by reacting an aliphatic, aromatic or araliphatic diisocyanate with a low-molecular compound having an active
20 hydrogen to obtain polyisocyanate and reacting the polyisocyanate with a blocking agent to make a mask. The diisocyanate includes tolylene diisocyanate, 4,4'-diphenylmethane isocyanate, xylylene diisocyanate, hexamethylene diisocyanate, 4,4'-methylene bis(cyclohexylisocyanate), methylcyclohexane diisocyanate, bis(isocyanatomethyl)cyclohexane,
25 isophorone diisocyanate, dimer acid diisocyanate, lysine diisocyanate, etc. The low-molecular compound having the active hydrogen includes water, ethylene glycol, propylene glycol, trimethylolpropane, glycerin, sorbitol, ethylenediamine, ethanolamine, diethanolamine, hexamethylenediamine, etc., and isocyanurate, uretdione, low-molecular weight polyester
30 containing a hydroxyl group, polycaprolactone, etc. The specific

example of the blocking agent includes alcohols such as methanol, ethanol, benzyl alcohol, etc., phenols such as phenol, cresol, etc., lactams such as caprolactam, butyrolactam, etc., oximes such as cyclohexanone, oxime, methylethylketoxime, etc. For instance, the specific example of
5 the blocked isocyanate includes ϵ -caprolactam-blocked isophorone diisocyanate (Vestagon B1530 made by Evonik Corporation, Crelan UI made by Bayer Corporation), etc.

[0049] In the powder coating composition according to the invention, the softening point of the isocyanate compound is preferably 10-120°C,
10 particularly preferably 40-100°C. When the softening point is less than 10°C, it is not preferable because the powder coating composition cures under an ordinary temperature environment or particulate masses can be formed. While, when the softening point exceeds 120°C, it is hard to disperse the isocyanate compound homogeneously in the powder coating
15 composition in the case of producing the powder coating composition through melt-kneading, so that the performance of a coat obtained such as smoothness, coat strength, humidity resistance, etc. can be impaired. The isocyanate compound preferably has 0.05-1.5 equivalents, particularly preferably 0.8-1.2 equivalents, of an isocyanate group based
20 on a hydroxyl group of the resin. When the isocyanate group is less than 0.05 equivalents, the curing degree of the powder coating composition is insufficient, so that the coat performance such as adhesion, coat hardness, resistance to chemicals, etc. can be made lower. While, when the isocyanate group exceeds 1.5 equivalents, there is a possibility that the
25 coat becomes brittle or resistances to heat, chemicals, humidity, etc. are inferior. Moreover, since the blocked isocyanate is expensive, the cost increases when the blocked isocyanate is used in excess.

[0050] <Luster pigment>

The powder coating composition according to the invention
30 can further comprise a luster pigment. Among them, there is a squamous

luster pigment. The luster pigment includes, for example, aluminum powder pigment, nickel powder pigment, gold powder, silver powder, bronze powder, copper powder, stainless powder pigment, mica pigment, graphite pigment, glass flake pigment, metal-coated glass powder, metal-coated mica powder, metal-coated plastic powder, and squamous iron oxide pigment, etc. In the powder coating composition according to the invention, the content of the luster pigment is preferably 0.1-30% by mass, more preferably 0.5-20% by mass. When the content of the luster pigment is less than 0.1% by mass, it is hard to obtain a sense of brightness of the coat, while when it exceeds 30% by mass, there is a possibility that the layer separation of the coat is inferior and the resistances of the coat to chemicals and humidity, etc. are inferior with the exposure of the luster pigment to the coat surface. Moreover, since the luster pigment is expensive, the cost increases when the luster pigment is used in excess.

[0051] <Color pigment, Extender pigment and Antirust pigment>

The powder coating composition according to the invention may comprise a commonly-used pigment, for example, a color pigment or an extender pigment, etc., besides the luster pigment. The color pigment includes, for example, an inorganic pigment such as titanium oxide, yellow oxide, titanium yellow, red oxide, lithopone, antimony oxide, etc., and an organic pigment such as Hansa yellow 5G, permanent yellow FGL, phthalocyanine blue, indanthrene blue RS, permanent red F5RK, brilliant fast scarlet G, etc. While, the extender pigment includes, for example, barium sulfate, barium carbonate, calcium carbonate, clay, silica powder, diatomaceous earth, talc, basic magnesium carbonate, alumina white, etc. Also, the powder coating composition according to the invention may comprise an antirust pigment when anticorrosion properties are necessary for a substrate to be coated. The antirust pigment includes, for example, condensed calcium phosphate, aluminum phosphate, condensed aluminum

phosphate, zinc phosphate, aluminum phosphite, zinc phosphite, calcium phosphite, zinc molybdate, calcium molybdate, manganese molybdate, etc. These pigments may be used alone or in a combination of two or more.

[0052] <Other additives>

5 The powder coating composition according to the invention may be compounded, if necessary, with a plasticizer, a cure accelerator, a cross-linking-promoting catalyst, a surface conditioner, an ultraviolet light absorber, a light stabilizer, an antioxidant, a flowability regulator, an anti-sagging agent and an anti-foaming agent, etc. as common
10 additives for coating materials.

[0053] <Ratio by mass of fluororesin to polyester resin>

 In the powder coating composition according to the invention, the ratio (A/B) by mass of the fluororesin (A) to the polyester resin (B) is preferably 50/50 to 10/90 from the viewpoint of weather resistance and
15 low cost. When the proportion of the fluororesin in the total of the fluororesin and the polyester resin exceeds 50% by mass, an expensive fluororesin is used in a larger amount, which results in a high cost. While, when the proportion of the fluororesin in the total of the fluororesin and the polyester resin is less than 10% by mass, weather
20 resistance cannot be sufficiently obtained.

[0054] <Solubility parameters of fluororesin and polyester resin>

 In the powder coating composition according to the invention, the difference in solubility parameter (SP value) between the fluororesin and the polyester resin is preferably 0.6-0.9. If the difference in SP
25 value between the fluororesin and the polyester resin is less than 0.6, when a coat is formed through melting and curing, the fluororesin can be compatibilized with the polyester resin, and it is hard for layer separation, like upper layer and lower layer, to take place. While, when the difference in SP value exceeds 0.9, the layer separation takes place, but
30 the delamination between the upper layer and the lower layer is a concern.

The solubility parameter, SP value, of a resin is calculated as follows: A resin is solved in tetrahydrofuran (THF) to prepare a 10 mass% solution. A certain amount of the solution is fractionated, and this volume (ml) is V_{THF} . The titration of the solution fractionated is carried out by dropping hexane (Hexane) and an ion-exchange water (Water), respectively, into the solution. The dropping amounts (ml) at the time when white turbidity takes place are V_{Hexane} and V_{Water} , respectively. The values obtained are substituted to the following equations (1) and (2) to calculate SP_n and SP_h . Next, the SP_n and SP_h calculated are substituted to the equation (3) to calculate SP value.

$$SP_n = (SP_{\text{THF}} \times V_{\text{THF}} + SP_{\text{Hexane}} \times V_{\text{Hexane}}) / (V_{\text{THF}} + V_{\text{Hexane}}) \cdots (1)$$

$$SP_h = (SP_{\text{THF}} \times V_{\text{THF}} + SP_{\text{Water}} \times V_{\text{Water}}) / (V_{\text{THF}} + V_{\text{Water}}) \cdots (2)$$

$$SP = 10^{((\log SP_n + \log SP_h) / 2)} \cdots (3)$$

(Note, however, that $SP_{\text{THF}}=9.1$, $SP_{\text{Hexane}}=7.3$, $SP_{\text{Water}}=23.4$)

15 **[0055]** <Curing>

In the case where the polyester resin reacts with the curing agent, the difference in temperature between the starts of melting and curing is preferably not less than 50°C, more preferably 80-100°C, under a condition of a temperature rising rate of 10°C/minute. If the difference in temperature is less than 50°C, it is easy to reduce the flow properties of the powder coating composition according to the invention when a coat is formed from the powder coating composition, and the image clarity of the coat, etc. can be reduced. The melting start temperature (°C) is a temperature at the time when the modulus of elasticity of a mixture of the polyester resin and the curing agent begins to lower, and the curing start temperature (°C) is a temperature at the time when the modulus of elasticity of the mixture begins to rise. Thus, in order to measure the difference in temperature, it is necessary to measure a change in the modulus of elasticity of the mixture of the polyester resin and the curing agent. The modulus of elasticity is measured with a

rheometer such as Rheometer ARES made by TA Instruments.

Conditions other than temperature rising rate are a parallel plate of 40 mm in diameter, a gap width of 1.0 mm, a frequency of 9.42 rad/s, a strain of 1.0%, a temperature range of 80-200°C.

5 **[0056]** When the temperature (°C) at which the fluoro-resin begins to react with the curing agent is a curing start temperature TR(A) and the temperature (°C) at which the polyester resin begins to react with the curing agent is a curing start temperature TR(B), the thermal difference TR(B)-TR(A) between the curing start temperatures TR(A) and TR(B) is
10 preferably not less than 15°C, more preferably not less than 20°C. If the thermal difference TR(B)-TR(A) is less than 20°C, when a coat is formed from the powder coating composition according to the invention, the layer separation can be deteriorated.

[0057] <Method for producing the powder coating composition>

15 The method for producing the powder coating composition according to the invention is a method for preparing the above-mentioned powder coating composition, and in particular, it is characterized by melt-kneading a mixture comprising the fluoro-resin, the polyester resin and the curing agent at 100-160°C, cooling and then pulverizing the
20 mixture to prepare a powder coating composition. Preferably, the powder coating composition can be obtained by dry-blending a mixture comprising the fluoro-resin, the polyester resin and the curing agent by means of a Henschel mixer, etc., melt-kneading it by means of a Ko-kneader, etc., cooling, pulverizing and thereafter classifying by means
25 of a woven metal wire of 180 meshes (96 μm), etc.

[0058] <Coat>

 The powder coating composition according to the invention is applied, for example, on the surface of a substrate composed of aluminum alloy for a building sash or a building panel, or steel stock, such as carbon
30 steel, of a railroad bridge, a road bridge, a gas tank, a petroleum tank, an

iron tower, etc., by a usual method, and then is melted and cured preferably at a temperature of 170-250°C, more preferably 170-210°C, to form a coat. In the powder coating composition according to the invention, the fluororesin and the polyester resin cause layer separation
5 without compatibilization, so that a coat can be formed which comprises a fluorine coating layer and a polyester coating layer. By segregation of the fluororesin and the polyester resin, the polyester coating layer is the lower layer side (that is, the side close to the surface of the substrate) and the fluorine coating layer is the upper layer side (that is, the side far from
10 the surface of the substrate). When the epoxy resin is used in the powder coating composition according to the invention, the epoxy resin is located in the lower layer side. The additives are oriented to the upper layer side of the coat.

EXAMPLES

15 **[0059]** The invention will be more particularly described below by the following Examples and Comparative Examples.

[0060] <Production of polyester resin A>

2652 g of neopentyl glycol as an alcohol component of a polyester resin, 3966 g of isophthalic acid as a carboxylic acid component
20 and 4.7 g of tetra-n-buty titanate as a reaction catalyst were charged into a stainless-steel reaction container provided with a stirring device, a heating device, a thermometer, a fractionating device and a nitrogen gas-introducing pipe, and the polycondensation reaction was carried out at 250°C for 16 hours while stirring under a nitrogen atmosphere. Once
25 a predetermined hydroxyl value was reached, the reaction was terminated to obtain a polyester resin A.

[0061] <Production of polyester resin B>

2496 g of neopentyl glycol as an alcohol component of a polyester resin, 4233 g of isophthalic acid as a carboxylic acid component
30 and 4.7 g of tetra-n-buty titanate as a reaction catalyst were charged into

a stainless-steel reaction container provided with a stirring device, a heating device, a thermometer, a fractionating device and a nitrogen gas-introducing pipe, and the polycondensation reaction was carried out at 250°C for 16 hours while stirring under a nitrogen atmosphere. Once
5 a predetermined hydroxyl value was reached, the reaction was terminated to obtain a polyester resin B.

[0062] <Production and evaluation of powder coating composition>

A raw material was mixed according to the compounding recipe shown in Tables 1-3, melted and kneaded at 130°C. The resulting
10 mixture was cooled and then pulverized to prepare a powder coating composition.

[0063] <Evaluation of powder coating composition>

The powder coating composition was subjected to various evaluation tests. The results are shown in Tables 4-6.

15 **[0064]** <Production of test plate>

A test plate was produced for the evaluation test of the powder coating composition. First, a chromate-treated aluminum plate of 1.5 mm in thickness was suspended in a vertical direction, and the aluminum plate was electrostatically coated at a voltage of -60 kV using corona
20 charging-type electrostatic powder coating equipment (made by Asahi Sunac Corporation, PG-1 type) so that the coat thickness is 60 µm. Next, it was baked in an electric furnace under a condition of 190°C×20 minutes and left to cool to room temperature to obtain a test plate.

[0065] <60° specular gloss>

25 It is measured using a glossmeter (micro-TRI-gloss made by BYK Corporation: incident and reflection angle of 60°) according to JIS K 5600-4-7.

[0066] <Coat's condition>

The condition of the surface of the coat after the production of
30 the test plate is determined in a visual manner.

- A ... No abnormality
- B ... Orange peel surface
- C ... Surface roughening
- D ... Graininess

5 **[0067]** <Layer separation properties>

The coat of the test plate is cut, and the cross section of the coat is observed by a microscope (Keyence Corporation) to evaluate whether the inside of the coat is separated into an upper layer and a lower layer. The cross section of the coat is also observed by a scanning
10 electron microscope (ultrahigh resolution scanning electron microscope SU-70 made by Hitachi High Technologies), and the distribution of fluorine element (fluororesin) in the cross section of the coat is confirmed by elemental analysis. As for Example 8, a mapping image of fluorine
15 atoms present in the cross section of the coat is shown in FIG. 1. The dense portion in the figure is a portion where fluorine element (fluororesin) exists in large numbers, which shows it is unevenly distributed to the upper layer.

· Layer separation properties (observation by a microscope)

- A ... Complete two-layer separation takes place.
- 20 B ... Partial two-layer separation takes place. That is, two-layer separation takes place, but there is a portion which has a coat thickness of less than one-half of the fluorine coating layer thickness of a complete two-layer separation.

C ... A polyester resin is exposed on the surface of the upper
25 layer.

· Layer separation properties (elemental analysis)

- A ... Fluorine element is unevenly distributed to the upper layer.
- B ... Fluorine element is unevenly distributed to the upper
30 layer, but it is also present in the lower layer.

C ... Fluorine element is present in the entire coat.

[0068] <Adhesion>

According to JIS K 5600-5-6 (cross-cut method), the coat is cut into 100 grids at one-millimeter intervals, and an adhesive tape is applied thereto to evaluate whether the subsequent peeling of the tape causes the coat to be peeled off. In the description of the tables, the denominator represents the number of the cross-cut grids (100) and the numerator represents the remaining number of grids in the test plate after peeling the tape.

10 **[0069]** <Resistance to weight falling>

In order to evaluate the resistance of the coat to a falling height of 50 cm in accordance with JIS K5600-5-3 (DuPont mode), the crack and peeling of the coat are observed with 500 g of weight and a center of impact of 1/2 inches ϕ .

15 **[0070]** <Boiling water resistance>

The test plate is immersed in an ion-exchange water ($95\pm 5^{\circ}\text{C}$) for 24 hours, cooled and then dried to evaluate the adhesion of the coat by a method in accordance with JIS K 5600-5-6 (cross-cut method). In the description of the tables, the denominator represents the number of the cross-cut grids (100) and the numerator represents the remaining number of grids in the test plate after peeling the tape.

[0071] <Mortar resistance>

A mortar paste is applied on the surface of the coat of the test plate and left to stand for 24 hours under a high-humidity environment of 50°C and 95 RH%. The mortar mass is peeled off from the test plate, which is washed with an ion-exchange water and thereafter the condition of the coat is evaluated in a visual manner.

[0072] <Nitric acid resistance>

The test plate is put on a glass bottle containing an aqueous solution of 70% by mass of nitric acid in such a way to put a lid on the

glass bottle. The coat surface of the test plate is exposed to steam for 60 minutes, then washed with an ion-exchange water and thereafter dried.

The color difference ΔE of the dried coat surface to the coat surface before exposure to steam is measured with a color difference meter

5 (CR-300 made by Minolta Corporation).

[0073] <Hydrochloric acid resistance>

10 drops of an aqueous solution of 10% by mass of hydrochloric acid are put on the coat surface of the test plate, which is covered by a watch glass as a lid. After 15 minutes, it is washed with an
10 ion-exchange water and thereafter dried. The condition of the dried coat is evaluated in a visual manner.

[0074] <Humidity resistance>

The test plate is left for 3000 hours under a high-humidity environment of 50°C and 95 RH%, washed with an ion-exchange water,
15 then left to cool and dried. Thereafter, the condition of the coat is evaluated in a visual manner.

[0075] <Salt water-spraying resistance>

The test plate is left to stand for 3000 hours under an environment of spraying salt water at 35°C, washed with an ion-exchange
20 water, then left to cool and dried. Thereafter, the condition of the coat is evaluated in a visual manner.

[0076] <Accelerated weathering resistance>

An accelerated weathering resistance testing machine is used in conformity to JIS B 7753 (sunshine weatherometer system), the test
25 time is 3000 hours, and the retention of 60° specular gloss before the test is 100%. The retention of 60° specular gloss after the test is measured by a glossmeter (micro-TRI-gloss made by BYK Corporation: incident and reflection angle of 60°) and the color difference ΔE before and after the test is measured with a color difference meter (CR-300 made by
30 Minolta Corporation).

[0077]

[Table 1]

		Table 1								
		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
Fluororesin	Parts by mass	7.0	13.0	21.0	28.0	35.0	35.0	34.0	35.0	17.0
Polyester resin A		63.0	52.0	49.0	42.0	35.0	35.0	34.0	35.0	17.0
Polyester resin B										
Acrylic resin A										
Acrylic resin B										
ϵ -caprolactam blocked isocyanate		23.0	22.0	22.0	21.0	20.0	20.0	20.0	20.0	10.0
β -hydroxyalkylamide										
Triglycidyl isocyanurate										
Epoxy resin		1.0	5.0	1.0	1.0	1.0		5.0	5.0	1.0
Surface conditioner		5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Color pigment		0.5	0.5	0.5	0.5	0.5	0.5	0.5		50.0
Luster pigment		3.0	3.0	3.0	3.0	3.0	3.0	3.0		
Total (parts by mass)		102.5	100.5	101.5	100.5	99.5	98.5	101.5	100.0	100.0

[0078]

5 [Table 2]

		Table 2								
		Example 10	Example 11	Example 12	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18
Fluororesin	Parts by mass	25.0	41.0	43.0	21.0	30.5	41.0	43.0	21.0	28.0
Polyester resin A		25.0	41.0	43.0	21.0	30.5	41.0	43.0	21.0	28.0
Polyester resin B										
Acrylic resin A										
Acrylic resin B										
ϵ -caprolactam blocked isocyanate		14.2								
β -hydroxyalkylamide			4.4	4.6	2.2	3.2				
Triglycidyl isocyanurate							5.6	5.9	2.9	3.8
Epoxy resin		1.0	5.0	5.0	1.0	1.0	5.0	5.0	1.0	5.0
Surface conditioner		5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Color pigment			0.5		50.0		0.5		50.0	
Luster pigment		30.0	3.0			30.0	3.0			30.0
Total (parts by mass)		100.2	99.9	100.6	100.2	100.2	101.1	101.9	100.9	99.8

[0079]

[Table 3]

Table 3

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Fluororesin	Parts by mass		35.0	43.0	42.0
Polyester resin A		70.0			
Polyester resin B					
Acrylic resin A			35.0	43.0	42.0
Acrylic resin B					
ϵ -caprolactam blocked isocyanate		24.0	20.0		
β -hydroxyalkylamide				4.6	
Triglycidyl isocyanurate					5.8
Epoxy resin		1.0	1.0	1.0	1.0
Surface conditioner		5.0	5.0	5.0	5.0
Color pigment		0.5	0.5	0.5	0.5
Luster pigment		0.1	3.0	3.0	3.0
Total (parts by mass)		100.6	99.5	100.1	99.3

[0080]

[Table 4]

Table 4

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
60° specular gloss	89	84	80	74	70	73	70	78	68
Coat's condition	A	A	A	A	A	A	A	A	B
Layer separation properties (observation by a microscope)	A	A	A	A	A	A	A	A	A
Layer separation properties (elemental analysis)	A	A	A	A	A	A	A	A	B
Adhesion	100/100	100/100	100/100	100/100	100/100	100/100	100/100	100/100	100/100
Resistance to weight filling	No crack No peeling	No crack No peeling	No crack No peeling	No crack No peeling	No crack No peeling	No crack No peeling	No crack No peeling	No crack No peeling	No crack No peeling
Boiling water resistance (coat's appearance)	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality
Boiling water resistance (adhesion)	100/100	100/100	100/100	100/100	100/100	100/100	100/100	100/100	100/100
Mortar resistance	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality
Nitric acid resistance (AE)	0.3	0.4	0.3	0.5	0.4	0.5	0.6	0.4	0.9
Hydrochloric acid resistance (appearance)	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality
Humidity resistance (appearance)	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality
Salt water-spraying resistance (appearance)	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality
Accelerated weathering resistance (glass retention)	88%	83%	82%	89%	88%	91%	75%	89%	79%
Accelerated weathering resistance (color difference ΔE)	0.9	0.5	1.0	0.8	0.5	0.4	1.5	0.3	0.8

5 [0081]

[Table 5]

Table 5

	Example 10	Example 11	Example 12	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18
60° specular gloss	76	76	79	72	79	78	79	70	76
Coat's condition	B	A	A	B	B	A	A	B	B
Layer separation properties (observation by a microscope)	A	A	A	A	A	A	A	A	A
Layer separation properties (elemental analysis)	B	A	A	B	B	A	A	B	B
Adhesion	100/100	100/100	100/100	100/100	100/100	100/100	100/100	100/100	100/100
Resistance to weight falling	No crack No peeling	No crack No peeling	No crack No peeling	No crack No peeling	No crack No peeling	No crack No peeling	No crack No peeling	No crack No peeling	No crack No peeling
Boiling water resistance (coat's appearance)	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality
Boiling water resistance (adhesion)	100/100	100/100	100/100	100/100	100/100	100/100	100/100	100/100	100/100
Mortar resistance	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality
Nitric acid resistance (ΔE)	0.9	0.7	0.6	0.7	0.8	0.5	0.7	0.9	1.0
Hydrochloric acid resistance (appearance)	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality
Humidity resistance (appearance)	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality
Salt water-spraying resistance (appearance)	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality	No abnormality
Accelerated weathering resistance (gloss retention)	81%	90%	89%	87%	83%	88%	90%	79%	83%
Accelerated weathering resistance (color difference ΔE)	0.7	0.6	0.5	0.9	0.8	0.7	0.4	0.9	1.0

[0082]

[Table 6]

Table 6

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
60° specular gloss	86	54	49	53
Coat's condition	A	C	C	C
Layer separation properties (observation by a microscope)	C	C	C	C
Layer separation properties (elemental analysis)	---	C	C	C
Adhesion	100/100	100/100	100/100	100/100
Resistance to weight falling	No crack No peeling	Cracks observed No peeling	Cracks observed No peeling	Cracks observed No peeling
Boiling water resistance (coat's appearance)	Slightly whitened	No abnormality	No abnormality	No abnormality
Boiling water resistance (adhesion)	100/100	100/100	100/100	100/100
Mortar resistance	Slightly whitened	No abnormality	No abnormality	No abnormality
Nitric acid resistance (ΔE)	1.5	1.7	1.5	1.8
Hydrochloric acid resistance (appearance)	No abnormality	No abnormality	Slightly whitened	No abnormality
Humidity resistance (appearance)	No abnormality	No abnormality	Slightly whitened	No abnormality
Salt water-spraying resistance (appearance)	No abnormality	No abnormality	No abnormality	No abnormality
Accelerated weathering resistance (gloss retention)	35%	52%	58%	48%
Accelerated weathering resistance (color difference ΔE)	2.1	2.2	1.8	2.3

5 [0083]

The raw material described in Tables 1-3 will be described below.

· Fluororesin

Trade name: Lumiflon LF710F (hydroxyl group-containing fluororesin) made by Asahi Glass Corporation, solubility parameter (SP

value) of 9.16

· Polyester resin A

Hydroxyl group-containing polyester resin, hydroxyl value of 45 mgKOH/g, number average molecular weight of 3200, weight average molecular weight of 13200, solubility parameter (SP value) of 9.99, melt viscosity of 3.1 Pa·s (190°C), gradient of 18425 in a range of 100-120°C in an Arrhenius plot on the basis of melt viscosity (Pa·s) measured under conditions of a measurement start temperature of 200°C and a temperature dropping rate of 10°C/minute

10 · Polyester resin B

Carboxyl group-containing polyester resin, acid value of 48 mgKOH/g, number average molecular weight of 3900, weight average molecular weight of 12300, solubility parameter (SP value) of 9.84, melt viscosity of 2.5 Pa·s (190°C), gradient of 15346 in a range of 100-120°C in an Arrhenius plot on the basis of melt viscosity (Pa·s) measured under conditions of a measurement start temperature of 200°C and a temperature dropping rate of 10°C/minute

· Acrylic resin A

ARUFON UH-2170 made by Toagosei Co., Ltd., hydroxyl group-containing acrylic resin, number average molecular weight of 4600, weight average molecular weight of 14000, solubility parameter (SP value) of 9.19, melt viscosity of 4.3 Pa·s (190°C), gradient of 12739 in a range of 100-120°C in an Arrhenius plot on the basis of melt viscosity (Pa·s) measured under conditions of a measurement start temperature of 200°C and a temperature dropping rate of 10°C/minute

· Acrylic resin B

ARUFON UC-3920 made by Toagosei Co., Ltd., carboxyl group-containing acrylic resin, number average molecular weight of 5800, weight average molecular weight of 15500, solubility parameter (SP value) of 9.32, melt viscosity of 4.8 Pa·s (190°C), gradient of 10498 in a

range of 100-120°C in an Arrhenius plot on the basis of melt viscosity (Pa·s) measured under conditions of a measurement start temperature of 200°C and a temperature dropping rate of 10°C/minute

· Luster pigment

5 Aluminum flake powder, trade name: PCF7620A made by Toyo Aluminium Corporation

· Color pigment

 Titanium oxide, trade name: TI-PURE R-960 made by DuPont Corporation

10 · Epoxy resin

 Trade name: EpoTohto DT-112 made by Tohto Kasei Co., Ltd.,

· ϵ -Caprolactam blocked isocyanate

 Isocyanate compound, trade name: Vestagon B1530 made by Evonik Degussa Corporation

15 · β -Hydroxyalkylamide

 Trade name: PRIMID XL-552 made by EMS-Griltech Corporation

· Triglycidyl isocyanurate

 Trade name: ARALDITE PT-810 made by Huntsman Corporation

· Surface conditioner

 Trade name: BYK-360P made by BYK-Chemie Corporation

· Difference in temperature between starts of melting and curing under condition of temperature rising rate of 10°C/minute

25 In the reaction of the polyester resin A and ϵ -caprolactam blocked isocyanate (isocyanate compound), the melting start temperature (softening point) was 95°C and the curing start temperature was 183°C under a condition of a temperature rising rate of 10°C/minute.

· Thermal difference TR(B) between curing start temperatures TR(A) and
30 TR(B)

The curing start temperature TR(A) at which the fluororesin began to react with ϵ -caprolactam blocked isocyanate (isocyanate compound) was 167°C, the curing start temperature TR(B) at which the polyester resin A began to react with ϵ -caprolactam blocked isocyanate
5 (isocyanate compound) was 182°C, and the thermal difference TR(B)-TR(A) was 15°C.

CLAIMS

1. A powder coating composition which is capable of forming a coat comprising a fluorine coating layer and a polyester coating layer, the powder coating composition comprising a fluoro-resin
5 containing a hydroxyl group or a carboxyl group, a polyester resin containing a hydroxyl group or a carboxyl group and a curing agent selected from the group consisting of β -hydroxyalkylamide, triglycidyl isocyanurate and an isocyanate compound.
2. A powder coating composition according to claim 1,
10 further comprising an epoxy resin.
3. A powder coating composition according to claim 1, further comprising a luster pigment.
4. A powder coating composition according to claim 1, wherein the polyester resin is a hydroxyl group-containing polyester resin
15 which has a number average molecular weight of not more than 5000 and a weight average molecular weight of 10000-20000.
5. A powder coating composition according to claim 1, wherein the polyester resin has a melt viscosity of not more than 3.5 Pa·s (190°C) and, in an Arrhenius plot on the basis of melt viscosity (Pa·s)
20 measured under conditions of a measurement start temperature of 200°C and a temperature dropping rate of 10°C/minute, has a gradient of not less than 15000 in a range of 100-120°C.
6. A powder coating composition according to claim 1, wherein the fluoro-resin is a hydroxyl group-containing fluoro-resin.
- 25 7. A powder coating composition according to claim 1, wherein a ratio (A/B) by mass of the fluoro-resin (A) to the polyester resin (B) is 50/50 to 10/90.
8. A powder coating composition according to claim 1, wherein a difference in solubility parameter (SP value) between the
30 fluoro-resin and the polyester resin is 0.6-0.9.

9. A method for producing a powder coating composition according to any one of claims 1-8, which comprises melt-kneading a mixture containing the fluororesin, the polyester resin and the curing agent at 100-160°C, cooling and then pulverizing the mixture to prepare a powder coating composition.
- 5