

COATED BODY

TECHNICAL FIELD

The present invention relates to a coated body provided with a base and a coating film that is arranged on a surface of the base, and to a coated body with excellent weather resistance, wear resistance and adherability.

BACKGROUND ART

In recent years, environmental issues of a global scale such as global warming, ozone layer destruction, acid rain and the like have received much attention, and there has been a call for international environmental measures, and along with this, from the viewpoint of environmental protection, various regulations have been made. Among these, the emission to the atmosphere of organic solvents (in particular, volatile organic compounds (VOCs)) has become a large problem, and along with the trend to strengthen the restriction of VOCs in various industries, there has been an active movement towards elimination of organic solvents (in particular VOC elimination). Also in the coating industry, as replacements for conventional organic solvent based coatings, there has been demand for environmentally friendly coatings which are completely free of VOCs, which do not require exhaust gas processing / waste water processing, and which can be recovered and reused, and there has been high anticipation for powder coatings.

Under such conditions, it has been proposed to use layer separation type powder coating compositions including a fluoro-resin having excellent weather resistance and a low cost polyester resin (for example, refer to Patent Documents 1 to 3).

Patent Document 1: Japanese Unexamined Patent Application, Publication No. 2011-12119

Patent Document 2: Japanese Unexamined Patent Application, Publication No. 2012-41383

Patent Document 3: Japanese Unexamined Patent Application, Publication No. 2013-76019

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

However, upon using layer separation type powder coating compositions such as those disclosed in Patent Documents 1 to 3, it was understood that coatings are formed which, as before, have room for improvement concerning the weather resistance, or coatings are formed which while ensuring weather resistance, have room for improvement concerning the wear resistance and adherability.

Thus, the objective of the present invention is to provide a coated body provided with a base and a coating film that is arranged on a surface of the base, and a coated body having excellent weather resistance, wear resistance, and adherability.

Means for Solving the Problems

In order to achieve the above mentioned objective, the present inventors carried out diligent research and as a result came to understand that these layer separation type powder coating compositions differ in the point of the compositional ratios of the resins constituting the fluororesin layer and the polyester resin layer formed after coating.

For example, in the layer separation type powder coating composition disclosed in Patent Document 2, the greater part of the resin components constituting the fluororesin layer situated on the upper side of the coating film is a fluororesin, and the greater part of the resin components constituting the polyester resin layer situated at the lower side is a polyester resin. Concerning the coating film formed by the layer separation type powder coating composition disclosed in Patent Document 2, because the compositions of the resin components constituting each layer differ greatly, it is not possible to obtain sufficient adherability between each layer, and it was understood that interlayer peeling can readily occur.

On the other hand, in the layer separation type powder coating composition disclosed in Patent Document 3, compared to the layer separation type powder coating composition disclosed in Patent Document 2, the ratio of the polyester resin as a resin component constituting the fluororesin layer is high, and the proportion of the fluororesin as a resin component constituting the polyester resin layer is high, and

the compositions of the resin components constituting each layer are relatively close. However, the ratio of the fluororesin constituting the fluororesin layer cannot be said to be sufficiently high from the viewpoint of weather resistance and wear resistance, and it was understood that there is room for improvement.

Thus, the present inventors, in order to solve these technical problems, discovered that it is possible to obtain a coated body with excellent weather resistance, wear resistance and adherability by adjusting to specified ranges the ratio of the fluororesin in the coating film surface, and the ratio of the fluororesin at a position where a depth from the coating film surface corresponds to half of the coating film thickness, and thus completed the present invention.

Namely, the coated body of the present invention is provided with a base and a coating film that is arranged on a surface of the base, wherein

the coating film is formed from a coating composition comprising at least a fluororesin and a resin other than the fluororesin,

a first fluorine concentration (mass%) is 30-50 mass% when the first fluorine concentration is defined as a ratio of fluorine atoms in a total mass of fluorine atoms and carbon atoms in a surface of the coating film, and

a mass ratio (A/B) of a second fluorine concentration (A) to the first fluorine concentration (B) is from 13/87 to 49/51 when T (μm) is defined as a film thickness of the coating film

and the second fluorine concentration is defined as a ratio of fluorine atoms in a total mass of fluorine atoms and carbon atoms at a position of a depth of $T/2$ (μm) from the surface of the coating film.

In a suitable example of the coated body of the present invention, the film thickness of the coating film is 40 to 200 μm .

In another suitable example of the coated body of the present invention, the base is a metal base.

In another suitable example of the coated body of the present invention, the resin other than the fluororesin is at least one resin selected from the group consisting of polyester resin and epoxy resin.

In another suitable example of the coated body of the present invention, the coating composition is a powder coating composition.

In another suitable example of the coated body of the present invention, the coating film has a scratch coefficient of 45 to 500.

Effects of the Invention

According to the present invention, by adjusting to specified ranges the ratio of the fluororesin at the coating film surface, and the ratio of the fluororesin at a position where the depth from the coating film surface corresponds to half of the coating film thickness, it is possible to provide a coated body having excellent weather resistance, wear resistance, and adherability.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

Below, the coated body of the present invention will be explained in detail. The coated body of the present invention is a coated body provided with a base and a coating film that is arranged on a surface of the base, wherein the coating film is formed from a coating composition comprising at least a fluororesin and a resin other than the fluororesin,

a first fluorine concentration (mass%) is 30-50 mass% when the first fluorine concentration is defined as a ratio of fluorine atoms in a total mass of fluorine atoms and carbon atoms in a surface of the coating film, and

a mass ratio (A/B) of a second fluorine concentration (A) to the first fluorine concentration (B) is from 13/87 to 49/51 when T (μm) is defined as a film thickness of the coating film and the second fluorine concentration is defined as a ratio of fluorine atoms in a total mass of fluorine atoms and carbon atoms at a position of a depth of T/2 (μm) from the surface of the coating film.

In the coated body of the present invention, it is required that a first fluorine concentration (mass%) is 30-50 mass% when the first fluorine concentration is defined as a ratio of fluorine atoms in a total mass of fluorine atoms and carbon atoms in a surface of the coating film. If the first fluorine concentration is within the above specified range, the ratio of the fluororesin in the coating film surface is sufficiently high, and therefore it is possible to improve the

weather resistance and wear resistance. In contrast, if the first fluorine concentration is below 30 mass%, sufficient weather resistance and wear resistance cannot be obtained. Further, the higher the first fluorine concentration, the more the weather resistance and wear resistance can be improved, but it is difficult to control the distribution of the fluororesin in the coating film such that the first fluorine concentration is higher than 50 mass% while still satisfying the stipulation concerning the second fluorine concentration.

In the present invention, the surface of the coating film is the surface positioned at the opposite side of the surface where the coating film contacts the base.

In the coated body of the present invention, a mass ratio (A/B) of a second fluorine concentration (A) to the first fluorine concentration (B) is required to be from 13/87 to 49/51, is preferably from 25/75 to 49/51, and is more preferably 30/70 to 45/55 when T (μm) is defined as a film thickness of the coating film and the second fluorine concentration is defined as a ratio of fluorine atoms in a total mass of fluorine atoms and carbon atoms at a position of a depth of T/2 (μm) from the surface of the coating film. If the mass ratio (A/B) is within the above specified range, regions where the composition ratios of the resin components in the coating film differ greatly (for example, the interface between the fluororesin layer and the polyester resin layer constituting the coating film disclosed in Patent Document 2) do not readily arise, and it is possible to sufficiently

maintain the adherability. Further, because a suitable concentration of fluorine is included in the vicinity of the middle of the inner portion of the film, it has suitable wear resistance.

Further, in the coated body of the present invention, the region where the ratio of the fluorine atoms in the total mass of fluorine atoms and carbon atoms is 30 to 50 mass% varies depending on the used fluororesin and its other compounding agents, but usually, it is a region closer to the coating film surface than the position where the depth is $T/2$ (μm). Therefore, if the second fluorine concentration, which is an indicator of the concentration of the fluorine resin at the position where the depth from the coating film surface is $T/2$ (μm), is within the above specified range, regions where the composition ratios of the resin components in the coating film differ greatly (for example, the interface between the fluororesin layer and the polyester resin layer disclosed in Patent Document 2) do not arise, and it is possible to sufficiently maintain the adherability.

In the present invention, the film thickness of the coating film is an average film thickness, and it can be determined, for example, by selecting 10 random locations of the coating film, carrying out film thickness measurements by optical microscopy, scanning electron microscopy or the like, and calculating their average value. Further, in the coated body of the present invention, the coating film is not a coating film obtained, for example, by coating a coating

composition comprising a resin other than the fluororesin, and then coating a coating composition comprising the fluororesin, but is a coating film obtained by coating a coating composition comprising a fluororesin and a resin other than the fluororesin, and therefore, the film thickness of the coating film is, for example, 40 to 200 μm .

In the present invention, the ratio of the fluorine atoms in the total mass of fluorine atoms and carbon atoms (the first fluorine concentration) in the surface of the coating film, and the ratio of the fluorine atoms at a position where the depth from the coating film surface corresponds to half of the coating film thickness (the second fluorine concentration) can be measured using an SEM/EDS (Scanning Electron Microscope / Energy Dispersive X-ray Spectroscopy) device.

In the case of measuring the first fluorine concentration, a method of measuring the ratio of fluorine atoms and carbon atoms by first observing the coating film surface by SEM, and then carrying out elemental analysis using EDS may be mentioned. Moreover, when observing the coating film surface by SEM, the value of the first fluorine concentration may fluctuate according to the SEM acceleration voltage, and in particular when the acceleration voltage is low, this tendency is large. Accordingly, measurements are preferably made with the acceleration voltage of the SEM set to 10 kV to 20 kV. Further, in order to reduce the damage of the coating film surface due to the electron beam accompanying the SEM measurement, a conductive material (for example, gold or the

like) is deposited on the measurement test piece surface prior to the measurement.

In the case of measuring the second fluorine concentration, first, the coating film cross section is observed by SEM. Next, by determining the ratio of the fluorine atoms and the carbon atoms at a position where the depth from the coating film surface corresponds to half of the coating film thickness from the linear distribution by EDS, it is possible to measure the second fluorine concentration. Moreover, when observing the coating film surface by SEM, the value of the second fluorine concentration may fluctuate according to the SEM acceleration voltage, and in particular when the acceleration voltage is low, this tendency is large. Accordingly, measurements are preferably made with the acceleration voltage of the SEM set to 10 kV to 20 kV. Further, in order to reduce the damage of the coating film surface due to the electron beam accompanying the SEM measurement, a conductive material (for example, gold or the like) is deposited on the measurement test piece surface prior to the measurement.

In the case of measuring the film thickness and the second fluorine concentration, the coating film cross section is observed, and generally, as the preparation method of the measurement test piece for observation of the coating film cross section, a method of preparing the measurement test piece by directly mechanically cutting, splitting or fracturing the coating film, and next, embedding this coating

film in a vertically standing state, in a resin such as an epoxy resin or the like, and after this, applying a treatment with a microtome or the like to shave, grind, or etch or the like, perpendicularly to the film surface, may be mentioned.

The coated body of the present invention, because the wear resistance of the coating film is high as described above, has a scratch coefficient of for example 45 to 500. Further, the scratch coefficient of the coating film can be measured as follows.

(Measurement Method)

The measurement can be made based on ASTM D968 (falling sand test method). Specifically, using a Gardner type falling sand abrasion tester, a test piece is disposed at a 45° inclination with respect to a horizontal plane, and silica sand #4 (average particle diameter: 0.6 to 1.2 mm) is dropped onto a central position of the coating film, and the scratch coefficient is calculated from the formula below. Further, the height of dropping the sand is 940 mm from the central position of the coating film.

$$\text{scratch coefficient} = V/T$$

[In the formula, V is the total amount of sand used in the dropped sand test (units: liters (L)), T is the value of subtracting the film thickness after the dropped sand test from the film thickness before the dropped sand test (namely, the abraded film thickness, units: μm).]

The coated body of the present invention is provided with a base and a coating film arranged on a surface of the base,

and the coating film is formed, for example, by coating a coating composition comprising at least a fluororesin and a resin other than the fluororesin, preferably a powder coating composition, on the surface of the base, and next, fusing/curing at a temperature preferably in a range of 170 to 250°C, more preferably in a range of 170 to 210°C. In the coated body of the present invention, the ratio of the fluororesin on the surface of the coating film, and the ratio of the fluororesin at a position where the depth from the coating film surface corresponds to half of the coating film thickness, are required to be adjusted within the above mentioned specified ranges, but in order to satisfy these stipulations, a combination of an acrylic surface conditioner and a wax is preferably blended into the above mentioned coating composition as described later.

The fluororesin used in the above mentioned coating composition is preferably a resin which is a solid at normal temperatures, and its softening point is preferably 50 to 150°C. In the coated body of the present invention, it is essential that the fluororesin provide weather resistance and wear resistance to the coating film. Further, normal temperatures is a range of temperatures of 20°C $\pm$ 15°C (5 to 35°C) as stipulated by JIS Z 8703.

Further, the above mentioned fluororesin preferably has a reactive site which reacts with curing agents and the like, and as the reactive site, it preferably comprises a hydroxyl group or a carboxyl group. A fluororesin comprising a hydroxyl

group or carboxyl group can be manufactured, for example, by copolymerizing a fluorine-containing monomer with a monomer comprising the specified reactive group.

As the above mentioned fluorine-containing monomer, for example, vinyl fluoride, vinylidene fluoride, trifluoroethylene, tetrafluoroethylene, bromotrifluoroethylene, chlorotrifluoroethylene, pentafluoropropylene, hexafluoropropylene, (per)fluoroalkyl trifluorovinyl ether [where the carbon number of the (per)fluoroalkyl group is 1 to 18] and the like may be mentioned.

On the other hand, the monomer comprising the specified reactive group is a polymerizable monomer comprising a hydroxyl group or a carboxyl group as a group which reacts with a crosslinking agent or the like (reactive group).

Specifically, as a hydroxyl group-containing polymerizable monomer, 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, and the like; hydroxyalkyl allyl ethers such as 2-hydroxyethyl allyl ether, 3-hydroxypropyl allyl ether, 4-hydroxybutyl allyl ether, 4-hydroxycyclohexyl allyl ether, and the like; hydroxyalkyl (meth)acrylates such as 2-hydroxyethyl (meth)acrylate and the like; esters of hydroxyalkyl carboxylic acids and vinyl alcohol such as vinyl hydroxyacetate, vinyl hydroxyisobutyrate, vinyl hydroxypropionate, vinyl hydroxybutyrate, vinyl hydroxyvalerate, vinyl hydroxycyclohexylcarbonate and the like;

esters of hydroxy acids such as hydroxypropanoic acid, hydroxybutanoic acid, hydroxypentanoic acid, hydroxy-2-methyl butanoic acid and the like, with allyl alcohols, and the like may be mentioned.

Further, as a carboxyl group-containing polymerizable monomer, monoesters of dicarboxylic acids and allyl alcohols, (meth)acrylic acids, carboxyalkyl (meth)acrylates, and the like may be mentioned.

Further, in the polymerization of the above mentioned fluororesin, a polymerizable monomer other than the above mentioned fluorine-containing monomer and monomer comprising a specified reactive group may be used. As such a polymerizable monomer, vinyl ethers, olefins, allyl ethers, vinyl esters, allyl esters, (meth)acrylic acid esters, amide (meth)acrylates, cyano group-containing monomers, dienes and the like, and crotonic acid esters and the like may be mentioned.

As specific examples of the polymerizable monomer other than the above mentioned fluorine-containing monomer and monomer comprising a specified reactive group, 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 and the like; olefins such as ethylene, propylene, 1-butene, isobutylene, cyclohexene, vinyl chloride, vinylidene chloride and the like; styrene-based monomers such as styrene, α -methylstyrene and the like; alkyl allyl ethers such as methyl allyl ether, ethyl allyl ether, butyl allyl ether, cyclohexyl allyl ether and the

like; vinyl esters of carboxylic acids (preferably fatty acids) such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, vinyl valerate, vinyl hexanoate, vinyl octanoate, vinyl versatate and the like; allyl esters of carboxylic acids (preferably fatty acids) such as allyl propionate, allyl acetate and the like; (meth)acrylic acid esters such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, cyclohexyl (meth)acrylate and the like; amido (meth)acrylates such as amido (meth)acrylate and the like; cyano group-containing monomers such as acrylonitrile, 2,4-dicyanobutene-1 and the like; dienes such as isoprene, butadiene and the like; crotonic acid esters such as 2-hydroxyethyl crotonate, 4-hydroxybutyl crotonate and the like, and the like may be mentioned.

The above mentioned fluoro-resins preferably have a fluorine content of 5 to 80 mass%, more preferably 10 to 70 mass%. Further, in the case that the above mentioned fluoro-resin is a hydroxyl group-containing fluoro-resin, the hydroxyl value of the fluoro-resin, from the viewpoint of maintaining the flexibility of the coating film, is preferably no greater than 100 mg KOH/g, on the other hand, from the viewpoint of imparting sufficient impact resistance to the coating film, is preferably no less than 10 mg KOH/g. In particular, the hydroxyl value of the fluoro-resin is preferably 30 to 70 mg KOH/g.

In the above mentioned coating composition, the content of the fluoro-resin is preferably 20 to 60 mass%.

The resin other than the fluororesin used in the above mentioned coating composition is preferably at least one resin selected from the group consisting of polyester resin and epoxy resin. Further, by the combined use of the resin other than the fluororesin, compared to the case of using only the fluororesin as the resin component, the appearance and processability of the coating film can be improved, and further, the manufacturing costs can be reduced. In the above mentioned coating composition, the content of the resin other than the fluororesin is preferably 25 to 64 mass%.

A polyester resin which can be used in the above mentioned coating composition can be manufactured by reacting a carboxylic acid component and a polyvalent alcohol component by a well known method. The above mentioned polyester resin is preferably a solid resin at normal temperatures, and its softening point is preferably 100 to 150°C. Further, the above mentioned polyester resin preferably has a reactive site which reacts with a curing agent or the like, and as the reactive site, it preferably comprises a hydroxyl group or carboxyl group.

As the carboxylic acid component which can be used in the manufacture of the above mentioned polyester resin, 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-nonane dicarboxylic acid, 1,10-decane dicarboxylic acid, 1,12-

dodecane dicarboxylic acid, 1,2-octadecane dicarboxylic acid, maleic acid, fumaric acid, cyclohexanedicarboxylic acid, hexahydrophthalic acid, tetrahydrophthalic acid, trimellitic acid, pyromellitic acid and the like, lower alkyl esters of these polyvalent carboxylic acids and their anhydrides; as well as hydroxycarboxylic acids such as malic acid, tartaric acid, 1,2-hydroxystearic acid, parahydroxybenzoic acid and the like, and the like may be mentioned.

As a polyvalent alcohol component which can be used in the manufacture of the above mentioned polyester resin, 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-cyclohexane dimethanol, trimethylolethane, trimethylolpropane, glycerin, pentaerythritol and the like may be mentioned.

The above mentioned polyester resin, as described above, can be manufactured using a carboxylic acid component and a polyvalent alcohol component as raw materials by a usual method known for manufacturing polyester resins for coating compositions. For example, the polyester resin can be manufactured by suitably combining the various raw materials mentioned above in the used blending ratios, and after carrying out esterification or an ester exchange reaction at 200 to 280°C by a usual method, a polycondensation reaction is carried out at 230 to 290°C using a catalyst under reduced

pressure, and as the case may be, after this, carrying out a depolymerization reaction using a polyvalent alcohol.

The above mentioned polyester resin may have a reactive group other than a hydroxyl group and carboxyl group. As such reactive sites, for example, functional groups such as amide groups, amino groups, nitrile groups, glycidyl groups, isocyanate groups and the like may be mentioned.

The above mentioned polyester resin, from the viewpoint of controlling the crosslinking reactions and coating film properties, is preferably a hydroxyl group-comprising polyester resin. Further, from the viewpoint of controlling the melt viscosity, the above mentioned polyester resin preferably has a number average molecular weight of no greater than 5000, and further, a weight average molecular weight of 10000 to 20000. Herein, the number average molecular weight and the weight average molecular weight can be determined by gel permeation chromatography (GPC) with polystyrene as a reference material.

In the case that the above mentioned polyester resin is a hydroxyl group-containing polyester resin, the hydroxyl value of the polyester resin is preferably 20 to 100 mg KOH/g, and more preferably 30 to 80 mg KOH/g. Further, the acid value of the above mentioned polyester resin is preferably 20 to 80 mg KOH/g, and more preferably 30 to 80 mg KOH/g.

In the case that the above mentioned coating composition includes a polyester resin, the content of the polyester resin in the above mentioned coating composition is preferably 25 to

64 mass%, and more preferably 25 to 63 mass%.

An epoxy resin which can be used in the above mentioned coating composition is preferably a solid resin at normal temperatures, and preferably has a softening point of 50 to 150°C. By using an epoxy resin, it is possible to improve the adherence to the base. The above mentioned epoxy resin is not particularly limited, and epoxy resins which have been conventionally used in epoxy resin coating compositions may be used.

As the above mentioned epoxy resin, specifically, for example, a bisphenol A type diglycidyl ether resin, a bisphenol F type diglycidyl ether resin, aminoglycidyl ether resin, bisphenol AD type diglycidyl ether resin, bisphenol Z type diglycidyl ether resin, O-cresol novolak epoxy resin, phenol novolak epoxy resin, biphenol glycidyl ether resin, cyclopentadiene skeleton epoxy resin, naphthalene skeleton epoxy resin, GMA acryl resin, as well as resins where the substituent groups other than the epoxy groups of these resins are substituted with other groups, for example, resins obtained by degeneration reactions such as degeneration reactions or esterification reactions using carboxyl group-terminated polybutadiene-acrylonitrile (CTBN) and the like, and the like may be mentioned. Further, the epoxy resins preferably have an epoxy equivalent of 300 to 1200, particularly preferably 400 to 1000.

In the case that the above mentioned coating composition includes an epoxy resin, the content of the epoxy resin in the

above mentioned coating composition is preferably 0.3 to 5 mass%.

The above mentioned coating composition preferably includes an acrylic surface conditioner and a wax. The detailed mechanism is unclear, but by blending an acrylic surface conditioner and a wax in the above mentioned coating composition, in addition to the effect that the surface tension of the coating composition becomes low and the fluororesin is more readily unevenly distributed at the coating film surface, the effect of preventing the viscosity of the coating composition from becoming large when melting after coating is manifest, and therefore, it becomes possible to easily adjust the ratio of the fluororesin at the coating film surface, and the ratio of the fluororesin at a position where the depth from the coating film surface corresponds to half of the coating film thickness to within the above mentioned specified ranges. Further, the acrylic surface conditioner and the wax may be separately blended into the raw materials of the coating composition, or a mixture obtained by mixing in advance the acrylic surface conditioner and the wax may be blended into the raw materials of the coating composition.

An acrylic surface conditioner which may be used in the above mentioned coating composition is a compounding agent which contributes to adjusting the surface of the coating film, and therefore has the property of melting at the temperatures used when forming the coating film. Therefore, the softening

point of the above mentioned acrylic surface conditioner is preferably 75 to 100°C. Further, in the present invention, the softening point of the acrylic surface conditioner can be measured according to the ring and ball softening point test method based on JIS K 2207 (2006). JIS K 2207 (2006) is originally a standard relating to petroleum asphalt, but it may also be applied to softening point measurement of an acrylic surface conditioner.

The above mentioned acrylic surface conditioner is preferably a copolymer obtained by copolymerizing a dibasic acid ester having a polymerizable unsaturated double bond (component X), at least one selected from an acrylic acid alkyl ester and a methacrylic acid alkyl ester (component Y), and optionally at least one of acrylic acid and methacrylic acid. Herein, as the dibasic acid ester, for example, a maleic acid diester such as maleic acid diethyl ester and the like, a maleic acid monoester, a fumaric acid diester such as fumaric acid diethyl ester and the like, a fumaric acid monoester and the like may be mentioned. As the acrylic acid alkyl ester, for example, normal butyl acrylate and the like may be mentioned. As the methacrylic acid alkyl ester, for example, normal butyl methacrylate and the like may be mentioned.

Further, the above mentioned acrylic surface conditioner is a copolymer of the component X and the component Y as described above for example, and therefore is a component which differs from core-shell type acrylic resin particles as described later.

In the case that the above mentioned coating composition includes an acrylic surface conditioner, the content of the acrylic surface conditioner in the above mentioned coating composition is preferably 0.5 to 6 mass%.

A wax that can be used in the above mentioned coating composition is preferably a wax with a melting point of no less than 40°C, and this wax more preferably has a melting point of 50°C to 100°C. Further, in the present invention, the melting point of the wax can be measured by a method of visual inspection as disclosed in JIS K 0064 (1992). As specific examples of such waxes, castor oil, amide compounds, polyolefins such as polyethylene and polypropylene and the like, ethylene-vinyl acetate copolymers, acrylic compounds such as ethylene-acrylic acid copolymers and the like, and the like may be mentioned. These waxes may be used individually, or may be used in combinations of two or more.

In the case that the above mentioned coating composition includes a wax, the content of the wax in the above mentioned coating composition is preferably 0.3 to 10 mass%. Further, in the above mentioned coating composition, a mass ratio (w/s) of the the wax (w) with respect to the acrylic surface conditioner is preferably 0.06 to 20.

The above mentioned coating composition preferably comprises a curing agent. The curing agent is not particularly limited provided that it is one which reacts with the fluororesin and the resin other than the fluororesin, and forms crosslinked bonds, and is preferably a curing agent

selected from the group consisting of β -hydroxyalkyl amides, triglycidyl isocyanurate, and isocyanate compounds. Further, in the case that the above mentioned coating composition includes a curing agent, the content of the curing agent in the above mentioned coating composition is preferably 2 to 25 mass%.

A β -hydroxyalkyl amide can be suitably used in the case that the resin component has a carboxyl group, and ones having two more functional groups per molecule are particularly preferable from the point of low temperature curability and the water resistance of the film obtained by coating. As the β -hydroxyalkyl amide, N,N-di(β -hydroxyethyl)acetoamide, bis(β -hydroxyethyl)adipoamide, bis(β -hydroxypropyl)adipoamide, bis[N,N-di(β -hydroxyethyl)]adipoamide, and bis[N,N-di(β -hydroxypropyl)]adipoamide are particularly preferable. The β -hydroxyalkyl amide preferably has 0.5 to 1.5 equivalents of hydroxylamide groups with respect to the carboxyl groups in the resin.

A triglycidyl isocyanurate can be suitably used in the case that the resin component has a carboxyl group. As the triglycidyl isocyanurate, for example, as product names, Araldite (registered trademark) PT 710, Araldite (registered trademark) PT 810, Araldite (registered trademark) PT 910, Araldite (registered trademark) PT 912 (all produced by Huntsman Advanced Materials Co., Ltd.), and the like may be mentioned. The triglycidyl isocyanurate preferably has 0.5 to 1.5 equivalents of the glycidyl group with respect to the

carboxyl groups in the resin.

An isocyanate compound can be suitably used in the case that the resin component has a hydroxyl group, and is more preferably a blocked isocyanate compound. The isocyanate compound is preferably a solid at normal temperatures. The isocyanate compound preferably has 0.05 to 1.5 equivalents of isocyanate groups with respect to the hydroxyl groups in the resin, and particularly preferably 0.8 to 1.2 equivalents.

Further, the above mentioned blocked isocyanate compound can be manufactured, for example, by reacting an aliphatic, aromatic, or aromatic-aliphatic diisocyanate with a low molecular compound having an active hydrogen, and reacting the obtained polyisocyanate with a blocking agent, and masking, and thus is easy to manufacture. Further, as the above mentioned diisocyanate, tolylene diisocyanate, 4,4'-diphenylmethane isocyanate, xylylene diisocyanate, hexamethylene diisocyanate, 4,4'-methylenebis(cyclohexyl isocyanate), methylcyclohexane diisocyanate, bis(isocyanatomethyl)cyclohexane, isophorone diisocyanate, dimer acid diisocyanate, lysine diisocyanate and the like, may be mentioned, and as the above mentioned low molecular compound having an active hydrogen, in addition to water, ethylene glycol, propylene glycol, trimethylol propane, glycerine, sorbitol, ethylenediamine, ethanolamine, diethanolamine, hexamethylenediamine and the like, isocyanurate, uretdione, low molecular polyesters comprising hydroxyl groups, polycaprolactone, and the like may be

mentioned. Further, as specific examples of the blocking agent, alcohols such as methanol, ethanol, benzyl alcohol and the like, phenols such as phenol, cresol and the like, lactams such as caprolactam, butyrolactam and the like, cyclohexanone, and oximes such as oxime, methyl ethyl ketoxime and the like, may be mentioned. For example, as specific examples of the blocked isocyanate, isophorone diisocyanate blocked by ϵ -caprolactam (Vestagon B1530 by Evonik, or Clairin UI by Bayer), and the like may be mentioned.

The above mentioned coating composition may also include core-shell type acrylic resin particles. By using core-shell type acrylic resin particles, it is possible to improve the processability of the coating film without decreasing the weather resistance.

The above mentioned core-shell type acrylic resin particles preferably have an average primary particle diameter, calculated by assigning the value of the specific surface area measured by the nitrogen gas adsorption method to the formula: $D = 6/(\alpha \times S)$ (wherein D is the average primary particle diameter (μm); α is the density (g/cm^3); and S is the specific surface area (m^2/g)), of 0.1 to 0.5 μm ; and further, an average secondary particle diameter measured by a laser diffraction / scattering type particle size distribution measurement device within a range of 5 to 50 μm .

The above mentioned core-shell type acrylic resin particles, at the particle surface, preferably have at least one functional group selected from the group consisting of

carbonyl group, hydroxyl group and glycidyl group.

The above mentioned core-shell type acrylic resin particles preferably have a multiphase structure consisting of a core layer with a glass transition temperature of no greater than 20°C which is an elastomeric polymer phase at room temperature, and a shell layer with a glass transition temperature of no less than 50°C which is a glassy polymer at room temperature. The core-shell type acrylic resin particles can be obtained, for example, by a first stage reaction which forms elastomeric polymer particles with a glass transition temperature of no greater than 20°C by emulsifying and suspension polymerizing a first polymerizable monomer which forms an elastomeric polymer phase, and subsequently, a second stage reaction of radical-polymerizing a polymerizable monomer which forms a glassy polymer phase with a glass transition temperature of no less than 50°C, under the presence of the above mentioned elastomeric polymer particles. Herein, in order to introduce a functional group onto the particle surface of the above mentioned core-shell type acrylic resin particles, the radical-polymerizable monomer which constitutes the glassy polymer preferably has at least one functional group selected from the group consisting of carboxyl groups, hydroxyl groups, and glycidyl groups.

The elastomeric polymer which constitutes the core layer is, for example, a polymer of unsaturated monomers which are useable in the synthesis of an elastomeric polymer. The glass transition temperature of the elastomeric polymer is

preferably no greater than 20°C, and more preferably in the range of -30 to -10°C. Herein, as specific examples of the unsaturated monomer, for example, alkyl (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate and the like; vinyl esters such as vinyl acetate and the like; vinyl halides or vinylidene halides such as vinyl chloride, vinyl fluoride, vinylidene chloride, vinylidene fluoride and the like; nitrogen-containing unsaturated monomers such as (meth)acrylonitrile, (meth)acryamide and the like; aromatic compounds such as styrene, α -methylstyrene, vinyl toluene and the like; hydroxyl group-containing unsaturated monomers such as hydroxyethyl (meth)acrylate, methylol (meth)acrylamide and the like; unsaturated carboxylic acids such as (meth)acrylic acid and the like; and diene monomers such as butadiene, isoprene and the like, and the like may be mentioned. These unsaturated monomers may be used individually, or may be used in combinations of two or more. As representative examples of the elastomeric polymer, poly(meth)acrylic acid ester rubber, polybutadiene rubber, polyisoprene rubber, polyvinyl chloride, styrene-butadiene rubber, styrene-butadiene-styrene rubber, styrene-isoprene-styrene rubber, styrene-butylene rubber, styrene-ethylene rubber, and ethylene-propylene rubber and the like may be mentioned. Among these, in particular, poly(meth)acrylic acid ester rubber, polybutadiene rubber, polyisoprene rubber, and styrene-butadiene rubber are

preferable.

The glassy polymer constituting the shell layer, for example, is a polymer of radical-polymerizable monomers adjusted such that the glass transition temperature is no less than 50°C, preferably in the range of 80 to 100°C. Herein, as the radical-polymerizable monomer, common vinyl monomers and the like may be used, and the above described unsaturated monomers and the like may be mentioned, but as vinyl monomers having the above mentioned functional groups, for example, esters of hydroxyalkyls with a carbon number of 2 to 8 with acrylic acid or methacrylic acid such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate and the like; monoesters of polyether polyols such as polyethylene glycol, polypropylene glycol, polybutylene glycol and the like with unsaturated carboxylic acids such as (meth)acrylic acid and the like; monoesters of polyether polyols such as polyethylene glycol, polypropylene glycol, polybutylene glycol and the like with hydroxyl group-containing unsaturated monomers such as 2-hydroxyethyl (meth)acrylate and the like; adducts of α,β -unsaturated carboxylic acids with monoepoxy compounds such as Cardura E10 (Shell Chemicals) or α -olefin epoxides; adducts of glycidyl (meth)acrylate with monobasic acids such as acetic acid, propionic acid, p-t-butylbenzoic acid, and fatty acids; monoester compounds or diester compounds of acid anhydride group-containing unsaturated compounds such as maleic anhydride or itaconic acid anhydride

with glycols such as ethylene glycol, 1,6-hexane diol, neopentyl glycol and the like; hydroxyalkyl vinyl ethers such as hydroxyethyl vinyl ether, hydroxyl group-containing monomers which include chlorine such as 3-chloro-2-hydroxypropyl (meth)acrylate, allyl alcohols, epoxy group-containing unsaturated monomers, and the like may be mentioned. These radical-polymerizable monomers may be used individually, or may be used in combinations of two or more.

The above mentioned core-shell type acrylic resin particles may be obtained by a conventional well known method, for example, an emulsion polymerization method or a suspension polymerization method or the like wherein, under the presence of a elastomeric polymer emulsion prepared in advance, a radical-polymerizable monomer and a radical polymerization initiator are added.

In the case that the above mentioned coating composition includes core-shell type acrylic resin particles, the content of the core-shell type acrylic resin particles in the above mentioned coating composition is preferably 0.1 to 5 mass%.

The above mentioned coating composition may also further include a luster pigment. Further, if a luster pigment is used, it is possible to improve the alkali resistance. Luster pigments are also available in the form of flakes. As the luster pigment, for example, an 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 flake shaped iron oxide pigment and the like may be mentioned.

The above mentioned coating composition, besides the luster pigment, may also comprise a commonly used pigment, for example, a coloring pigment or an extender pigment or the like. As a coloring pigment, for example, inorganic pigments such as titanium oxide, yellow iron oxide, titan yellow, Bengala, lithopone, antimony oxide and the like, organic pigments such as Hansa yellow 5G, permanent yellow FGL, phthalocyanine blue, indanthrene blue RS, permanent red F5RK, brilliant fast scarlet G and the like, and the like may be mentioned. On the other hand, as an extender pigment, for example, barium sulfate, barium carbonate, calcium carbonate, clay, silica powder, diatomaceous earth, talc, basic magnesium carbonate, alumina white and the like may be mentioned. Further, in the case that corrosion resistance is required for the base to be coated, the above mentioned coating composition may include an anticorrosive pigment. As the anticorrosive pigment, for example, condensed calcium phosphate, aluminum phosphate, condensed aluminum phosphate, zinc phosphate, aluminum phosphite, zinc phosphite, calcium phosphite, zinc molybdate, calcium molybdate, manganese molybdate and the like may be mentioned. These pigments may be used individually, or may be used in combinations of two or more.

In the case that the above mentioned coating composition includes pigments, the total content of the pigments in the

above mentioned coating composition is preferably 0.2 to 35 mass%.

Further, in the above mentioned coating composition, as commonly used additives for coating compositions, plasticizers, curing accelerators, crosslinking accelerator catalysts, ultraviolet absorbers, light stabilizers, antioxidants, fluidity conditioners, anti-sagging agents, antifoaming agents and the like may also be blended as required.

As the production method of the above mentioned coating composition, for example, a method of preparing a powder coating composition by melt kneading a mixture comprising the above mentioned fluororesin, resin other than the fluororesin, acrylic surface conditioner, and wax at 100 to 160°C, and after cooling this mixture, pulverizing, may be mentioned. Preferably, the powder coating composition can be obtained by dry blending the mixture comprising the above mentioned fluororesin, resin other than the fluororesin, acrylic surface conditioner, and wax with a Herschel mixer or the like, and after this, melt mixing using a co-kneader or the like at 120 to 140°C, cooling, and pulverizing, and after this, classifying using a 180 mesh (96 μm) wire mesh or the like.

As the coating method of the above mentioned coating composition, for example, corona discharge type electrostatic powder coating, frictional charging type electrostatic powder coating, fluidized bed type powder coating, electrostatic fluidized bed type powder coating, electric field cloud type powder coating, and the like may be mentioned. After the

coating, the coating film is formed by melting/curing the coating composition at a temperature preferably in the range of 160 to 250°C, and more preferably in the range of 170 to 220°C.

As the base constituting the coated body of the present invention, for example, a metal base such as steel, zinc, aluminum, copper, tin and the like may be mentioned, and in order to improve the adherability with respect to the coating film, the surface of the metal base is preferably subjected to a priming treatment. Further, the base may be present in many forms depending on its intended purpose, for example, a plate shape or the like may be mentioned, and the coating film constituting the coated body of the present invention is usually formed on one surface of the base.

As specific examples of the coated body of the present invention, transportation equipment such as automobiles, trains, airplanes and the like, and their components, bridges and their components, pylons and their components, industrial hardware such as engineering components, waterproof sheets, tanks, pipes and the like, building components such as building exteriors, doors, window components, monuments, polls and the like, road components such as road median strips, guardrails, noise barriers, polycarbonate translucent plates, traffic lights and the like, telecommunication equipment and their components, home appliances, electric and electronic components and the like may be mentioned.

EXAMPLES

Below, the present invention is explained in further detail with reference to examples, but the present invention is not in any way limited by these examples.

Production Example of the Acrylic Surface Conditioner
(Acrylic Surface Conditioner A)

300 parts by mass of butyl acetate were added into a polymerization apparatus provided with circulating condenser cooler, thermometer, stirring mechanism, and drip tank, and the instilled solution A shown below was instilled for about 3 hours at 110°C under a nitrogen atmosphere. After completing the instillation, 5 parts by mass of t-amylperoxy-2-ethylhexanoate were added and this was held for 2 hours at 110°C. After this, the temperature was increased to 130°C, the butyl acetate was distilled under reduced pressure, and the acrylic surface conditioner A was obtained. The polystyrene converted number average molecular weight of the acrylic surface conditioner A as measured by gel permeation chromatography was 3500. Further, the softening point of the acrylic surface conditioner A as measured by the ring and ball softening point test method based on JIS K 2207 (2006) was 83°C.

Instilled solution A: a solution consisting of 324 parts by mass of normal butyl acrylate, 65 parts by mass of acrylic acid, 28 parts by mass of maleic acid diethyl ester, 15 parts by mass of t-amylperoxy-2-ethylhexanoate, and 200 parts by mass of butyl acetate.

(Acrylic Surface Conditioner B)

Other than using the instilled solution B instead of the instilled solution A, the acrylic surface conditioner B was obtained in the same way as the production example of the acrylic surface conditioner A. The polystyrene converted number average molecular weight of the acrylic surface conditioner B as measured by gel permeation chromatography was 4100. Further, the softening point of the acrylic surface conditioner B as measured by the ring and ball softening point test method based on JIS K 2207 (2006) was 92°C.

Instilled solution B: a solution consisting of 324 parts by mass of normal butyl acrylate, 65 parts by mass of acrylic acid, 28 parts by mass of fumaric acid diethyl ester, 15 parts by mass of t-amylperoxy-2-ethylhexanoate, and 200 parts by mass of butyl acetate.

(Acrylic Surface Conditioner C)

Other than using the instilled solution C instead of the instilled solution A, the acrylic surface conditioner C was obtained in the same way as the production example of the acrylic surface conditioner A. The polystyrene converted number average molecular weight of the acrylic surface conditioner C as measured by gel permeation chromatography was 2900. Further, the softening point of the acrylic surface conditioner C as measured by the ring and ball softening point test method based on JIS K 2207 (2006) was 78°C.

Instilled solution C: a solution consisting of 324 parts by mass of normal butyl acrylate, 47 parts by mass maleic acid

diethyl ester, 46 parts by mass of fumaric acid diethyl ester, 15 parts by mass of t-amylperoxy-2-ethylhexanoate, and 200 parts by mass of butyl acetate.

Production Example of the Powder Coating Composition

The raw materials according to the formulations shown in Table 1 were added into a high speed mixer and blended for 1 min. Next, the obtained mixture was kneaded using a twin screw mixer (made by Toshiba) set to a temperature of 120°C, and the discharged kneaded substance was cooled with a cooling roll, and after this, pulverized using a pin mill, classified using a 180 mesh screen, and the powder coating compositions (50% volume average particle diameter: 32 μm) of Examples 1 to 11 and Comparative Examples 1 to 3 were obtained.

Production Example of Coated Body

Test plates (coated bodies) were prepared using the powder coating compositions of Examples 1 to 11 and Comparative Examples 1 to 3. Specifically, chromic acid chromate treated aluminum plates with a plate thickness of 1.5 mm were vertically suspended, and were electrostatically coated using a corona discharge type electrostatic powder coating device (Model PG-1 of Asahi Sanac) with a voltage of -60 kV such that the film thickness became 60 μm , firing was carried out in an electric oven under conditions of 190°C x 20 min, and allowed to cool as-is to room temperature to produce the test plates.

Evaluation

Various measurements and evaluation tests were carried

out for the obtained test plates, and the results thereof are shown in Table 1.

Measurement Method of the Film Thickness

The test plates were vertically stood in a clear cup for embedding using sample clips, an epoxy resin "epocure (Bueler Co.) base compound + curing agent" was poured in, the epoxy resin was allowed to completely cure, and test plates embedded in the epoxy resin were obtained. Using a grinder "Ecomet 3000 + Automet 2000 (Bueler Co.)", sandpaper #320 and #600 and buffing metadyne, master prep (Bueler Co.) was poured, and grinding of the test plates embedded in the epoxy resin was carried out, and cross sections of the coating films were obtained. For the obtained coating film cross sections, the film thickness was measured at 10 points using an SEM (Hitachi High Technologies SU-70) with an acceleration voltage of 1 kV, and a magnification of 900 times, and the average film thickness was determined.

Measurement Method of the Mass Ratio of the Fluorine Atoms and Carbon Atoms

As the measurement apparatus, the SEM used was a Hitachi High Technologies SU-70, and the EDS used was an INCA X-Sight (Model 7969) by Oxford Instruments. With the EDS, the conditions were set with cobalt selected as the quantitative optimization element. At this time, the device parameters were Livetime 100 seconds, Process time 5, Spectrum Range 0 - 20 kev, Number of channels 1K.

(Measurement Method of the First Fluorine Concentration)

The first fluorine concentration is the ratio (mass%) of the fluorine atoms in a total mass of fluorine atoms and carbon atoms in the surface of the coating film. First, a slice of about 1 cm x 1 cm of the test plate was cut off, and gold was vapor deposited onto this cut-off sample in order to reduce the damage to the coating film surface by the electron beam, and after fixing this gold-deposited cut-off sample to the observation platform of the SEM with conductive tape, SEM observation was carried out with an acceleration voltage of 15 kV, and a magnification of 500 times. Next, a surface area of 245 μm x 185 μm of the coating film surface was arbitrarily selected by EDS, elemental mapping measurement was carried out for this coating film surface, the ratio of the carbon atoms and the fluorine atoms was measured, and the ratio of the fluorine atoms in a total mass of fluorine atoms and carbon atoms was determined. After this, the location for carrying out the elemental mapping measurement was changed, and the ratio of the fluorine atoms in a total mass of fluorine atoms and carbon atoms in a coating film surface (245 μm x 185 μm) was measured nine times. The average value of the ten measurement results was taken as the first fluorine concentration.

(Measurement Method of the Second Fluorine Concentration)

The second fluorine concentration is the ratio of the fluorine atoms (mass%) in a total mass of fluorine atoms and carbon atoms at a position where the depth from the coating film surface corresponds to half of the coating film thickness.

First, the test plate embedded in the epoxy resin used for the coating film thickness measurement was gold-deposited to reduce damage to the coating film surface by the electron beam, and after fixing this gold-deposited sample to the observation platform of the SEM with conductive tape, SEM observation was carried out with an acceleration voltage of 15 kV and a magnification of 900 times. Next, at a position where the depth from the coating film surface corresponds to half of the coating film thickness, a line parallel to the coating film surface and with a length of 135 μm is arbitrarily selected, elemental mapping measurement of this line (linear distribution) is carried out by EDS, the ratio of the carbon atoms and the fluorine atoms is measured, and ratio of the fluorine atoms in a total mass of fluorine atoms and carbon atoms was determined. After this, the position for carrying out the elemental mapping measurement was changed, and the ratio of the fluorine atoms in a total mass of fluorine atoms and carbon atoms at a position where the depth from the coating film surface corresponds to half of the coating film thickness is measured nine times. The average value of the ten measurement results was taken as the second fluorine concentration.

Wear Resistance

Measured according to ASTM D968 (falling sand test method). Specifically, using a Gardner type falling sand abrasion tester, the test plate was disposed at a 45° inclination with respect to a horizontal plane, silica sand #4

was dropped onto a central position of the coating film, and the scratch coefficient was calculated from the formula below. Further, the height of dropping the sand was 940 mm from the center position of the coating film.

$$\text{scratch coefficient} = V/T$$

[In the formula, V is the total amount of sand used in the dropped sand test (units: liters (L)), T is the value of subtracting the film thickness after the dropped sand test from the film thickness before the dropped sand test (namely, the worn film thickness, units: μm).]

Further, based on the calculated scratch coefficient, the wear resistance was evaluated based on the following evaluation standards.

- ...scratch coefficient of 100 or more
- ...scratch coefficient of no less than 45 to less than 100
- △...scratch coefficient of no less than 40 to less than 45
- ×...scratch coefficient of less than 40.

Weather Resistance

The test plates (coated bodies) obtained using the powder coating compositions of Examples 1 to 11 and Comparative Examples 1 to 3 were subjected to weather resistance evaluation using an accelerated weather resistance testing apparatus based on JIS B7753 (sunshine weatherometer system). Further, the test time was 3000 hours. The 60° specular gloss value before and after the 3000 hour test was measured with a glossmeter (mirco-TRI-gloss by BYK; input reflection angle 60°), the rate of change of the 60° specular gloss value after

the 3000 hour test with respect to the 60° specular gloss value before the 3000 hour test was determined, and the weather resistance was evaluated according to the below evaluation standards.

○...rate of change of no less than 90%

○...rate of change of no less than 70% to less than 90%

△...rate of change of no less than 50% to less than 70%

×...rate of change of less than 50%.

Adherability

Based on JIS K5600-5-6 (crosscut method), the coating film of the test plates was cut into 100 square grid-shaped pieces at 1 mm intervals, a peel strength test was carried out using an adhesive tape, the residual rate after the peel strength test was determined, and the adherability was evaluated according to the below evaluation standards.

○: 100/100 (number of cut portions remaining after the test / total number of cut portions before the test)

△: 85/100 to 99/100

×: 84/100 or less

[Table 1]

Table 1

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11
fluororesin (*1) polyester resin (*2) epoxy resin (*3) titanium oxide crosslinked resin particles (*8) core-shell type acrylic resin particles (*9) curing agent (*4) silica based surface conditioner (*5) acrylic surface conditioner A (*6) acrylic surface conditioner B (*6) acrylic surface conditioner C (*6) wax (*7) total		24	37	23	24	24	37	37	37	37	37	37	37	37	37
		50	37	23	50	50	37	37	37	37	37	37	37	37	37
		1		2	1	1	1	1	1	1	1	1	1	1	1
		0.5	0.5	30	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
				5											
		0.1	0.1		0.1	0.1	0.1	0.1	0.1			0.1	0.1	0.1	0.1
		18	18	13	18	18	18	18	18	18	18	18	18	18	18
		5	5	5											
					0.5	5	0.5	3	5	0.5	5				
												0.5	5		
		98.6	97.6	101	94.5	99.6	94.5	97.2	99.6	94.4	99.5	94.5	99.6	94.5	99.6
first fluorine concentration (mass%)		24	28	28	31	34	32	40	45	35	45	32	45	32	45
second fluorine concentration / first fluorine concentration (mass% / mass%)		26/73	33/67	5/95	24/76	23/77	32/68	31/69	29/71	16/84	20/80	32/68	29/71	32/68	29/71
film thickness (μm)		65	58	63	57	58	57	66	63	65	62	64	64	61	63
wear resistance	scratch coefficient	42	41	43	64	126	74	146	158	71	143	87	142	69	119
	evaluation	Δ	Δ	Δ	$\circ$	$\circ\circ$	$\circ$	$\circ\circ$	$\circ\circ$	$\circ$	$\circ\circ$	$\circ$	$\circ\circ$	$\circ$	$\circ\circ$
weather resistance	rate of change	58%	72%	83%	78%	86%	77%	92%	95%	85%	79%	83%	92%	72%	94%
	evaluation	Δ	$\circ$	$\circ$	$\circ$	$\circ$	$\circ$	$\circ\circ$	$\circ\circ$	$\circ$	$\circ$	$\circ$	$\circ\circ$	$\circ$	$\circ\circ$
adherability	residual rate	100/100	100/100	89/100	100/100	100/100	100/100	100/100	100/100	100/100	100/100	100/100	100/100	100/100	100/100
	evaluation	$\circ$	$\circ$	Δ	$\circ$	$\circ$	$\circ$	$\circ$	$\circ$	$\circ$	$\circ$	$\circ$	$\circ$	$\circ$	$\circ$

Further, the details of the raw materials disclosed in Table 1 are shown below.

(*1) Fluororesin (Asahi Glass, product name: Lumiflon LF710F, hydroxyl group-containing fluororesin)

(*2) Polyester resin (Daicel-Allnex LTD., product name: Crylcoat 4642-3)

(*3) Epoxy resin (Tokyo Kasei, product name: Epotote DT-112)

(*4) Curing agent (ϵ -caprolactam block isocyanate, Evonik Degussa, product name: Bestagon B1530)

(*5) Silica based surface conditioner (BYK Japan K.K., product name: BYK360P)

(*6) The acrylic surface conditioners A to C obtained in the above described production examples of the acrylic surface conditioner were used.

(*7) Wax (castor oil, melting point 80°C, Itoh Oil Manufacture, product name: Castor Curing Oil)

(*8) The crosslinked resin microparticles produced by the method below were used.

(*9) The core-shell type acrylic resin particles produced by the method below were used.

(Production Example of the Crosslinked Resin Microparticles)

Below, the production method of the crosslinked resin microparticles shown in Table 1 is explained. Using a homomixer (Mizuho Industrial Co., tabletop type quick homomixer LR), with a rotation rate of 12000 rpm, the oil phase shown below was dispersed in the aqueous phase shown below. This dispersed solution was added into a polymerization

reaction vessel equipped with a stirring mechanism, heating device and thermometer, and suspension polymerization was carried out while continuing stirring at 60°C for 6 hours. This suspension was filtered at reduced pressure, and the obtained reaction product was washed with water, dried, and pulverized, and crosslinked resin microparticles with a volume average particle diameter of 6.8 μm were obtained.

•Oil Phase

butyl acrylate, 80 parts by mass

tetradecaethyleneglycol dimethacrylate, 20 parts by mass

benzoyl peroxide, 0.3 parts by mass

•Aqueous Phase

deionized water, 400 parts by mass

polyvinyl alcohol (saponification degree 85%), 8 parts by mass

sodium lauryl sulfate, 0.07 parts by mass

(Production Example of the Core-Shell Type Acrylic Resin Particles)

Below, a production example of the core-shell type acrylic resin particles shown in Table 1 is explained.

1500 g of deionized water and 300 g of 5 vol% polyvinyl alcohol aqueous solution were added to a 5 L capacity polymerization vessel, and using a homomixer (As One Co.), while stirring at 4500 rpm, 576 g of n-butyl acrylate, 12 g of 1,4-butyleneglycol diacrylate, 12 g of allyl methacrylate, and 6 g of lauryl peroxide (polymerization initiator) were dissolved and the obtained monomer mixed solution was added in

block, dispersion treatment was carried out for 1 hr, and a monomer dispersed solution was obtained. Next, a stirring mechanism and a reflux condenser were attached to this reaction vessel, and under a flow of nitrogen gas, while stirring, the temperature was raised to 70°C. The reaction was carried out for 2 hrs at 70°C while stirring. At this point in time, sampling was carried out from the suspended solution of the obtained polymer particles, and when the monomer polymerization conversion rate was measured, it was 94%. Next, the suspended solution of the obtained polymer particles was cooled to 60°C. While stirring this suspended solution at 4500 rpm, a monomer emulsified solution was continuously added over 15 min for the second stage reaction shown below. (The monomer emulsified solution for the second stage reaction was prepared by mixing 352 g of methyl methacrylate, 40 g of ethyl acrylate, 10 g of 2-hydroxyethyl methacrylate, 8 g of ethyleneglycol dimethacrylate, 4 g of 2,2'-azo-bis-isobutyronitrile, 100 g of 1 mass% sodium dodecylsulfonate aqueous solution, and 100 g of deionized water.)

The polymerization was initiated, at the point in time that the generated heat was observed and measured, the temperature increased to 80°C, and an aging reaction was carried out for 3 hours. After cooling the obtained suspended solution to room temperature, it was dehydration washed using a centrifuge, and further, left at 60°C for one day and night, blow dried, and the core-shell type acrylic resin particles were obtained.

From the DSC measurement of the core-shell type acrylic resin particles, the glass transition temperature of the elastomeric polymer phase (core layer) was -20°C , and the glass transition temperature of the glassy polymer phase (shell layer) was 83°C . The average primary particle diameter calculated from the specific surface area measurement measured with an ASAP 2020 (Shimadzu Co.) specific surface area / pore distribution measurement device was $0.1\text{ }\mu\text{m}$, and the average secondary particle diameter measured with a Partica LA-950V2 (Horiba) laser diffraction / scattering type particle size distribution measurement device was $6\text{ }\mu\text{m}$.

CLAIMS

1. A coated body provided with a base and a coating film arranged on a surface of the base, wherein

the coating film is formed from a coating composition comprising at least a fluororesin, and a resin other than the fluororesin,

a first fluorine concentration (mass%) is 30-50 mass% when the first fluorine concentration is defined as a ratio of fluorine atoms in a total mass of fluorine atoms and carbon atoms in a surface of the coating film; and

a mass ratio (A/B) of a second fluorine concentration (A) to the first fluorine concentration (B) is from 13/87 to 49/51 when T (μm) is defined as a film thickness of the coating film and the second fluorine concentration is defined as a ratio of fluorine atoms in a total mass of fluorine atoms and carbon atoms at a position of a depth of T/2 (μm) from the surface of the coating film.

2. The coated body according to claim 1, wherein the film thickness of the coating film is 40 to 200 μm .

3. The coated body according to claim 1 or 2, wherein the base is a metal base.

4. The coated body according to any one of claims 1 to 3, wherein the resin other than the fluororesin is at least one

resin selected from the group consisting of polyester resin and epoxy resin.

5. The coated body according to any one of claims 1 to 4, wherein the coating composition is a powder coating composition.

6. The coated body according to any one of claims 1 to 5, wherein the coating film has a scratch coefficient of 45 to 500.