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(54) METHOD FOR APPLYING THERMOSETTING FLUORORESIN POWDER COATING

(57) A method of coating a thermosetting fluorine-containing resin powder coating composition by electrostatic coating, in which an article to be coated is previously heated to a temperature in a range higher than a glass transition temperature of the powder coating composition and up to a temperature higher than a curing starting temperature by 10°C. According to this coating method, since an adhesion efficiency per one coating is enhanced, the number of coats until a desired coating thickness is obtained can be decreased and productivity is enhanced. Also since a smoothness of a surface of coating film is excellent, a coated article having good appearance can be provided.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a coating method characterized by pre-treatment of an article to be coated by electrostatic coating of a thermosetting fluorine-containing resin powder coating composition.

BACKGROUND ART

[0002] Recently powder coating compositions have been widely used in the whole field of coating of metals from the viewpoint of many advantages that no pollution arises because there is no exhausting of a volatile solvent, maintenance of a coating line is easy, etc. as compared with general solvent-based coating compositions. In the powder coating compositions, there are thermoplastic powder coating compositions prepared by using thermoplastic resins (JP-A-9-302306, etc.) and thermosetting powder coating compositions prepared by using thermosetting resins. Further in the thermosetting powder coating compositions, there are known those comprising a general-purpose resin such as polyester, acrylic resin or epoxy resin as a resin component and those comprising a thermosetting fluorine-containing resin as a resin component (JP-B-6-104792, etc.).

[0003] With respect to a coating method of powder coating compositions, a fluidized bed coating method and an electrostatic coating method are known. The fluidized bed coating method is a method of coating by dipping a heated substrate into a powder coating composition, and in many cases, is used for thick coating of thermoplastic powder coating compositions. The electrostatic coating method is a method of spraying a statically charged powder coating composition onto a substrate and in many cases, is used for thermosetting powder coating compositions.

[0004] Among the thermosetting powder coating compositions, the thermosetting fluorine-containing resin powder coating composition is easily subject to electric repellence between the particles of powder coating composition due to a high static charge inherent to the fluorine-containing resin to lower an adhesion efficiency of the coating composition, unlike general-purpose resin powder coating compositions. With respect to those problems of the thermosetting fluorine-containing resin powder coating composition, means to-solve them are not known. For example, JP-B-6-104792 discloses an electrostatic coating method of a thermosetting fluorine-containing resin powder coating composition, but there is no suggestion as to improvements in an adhesion efficiency and a coating method.

[0005] An object of the present invention is to provide an electrostatic coating method for improving the both of an adhesion efficiency of a thermosetting fluorine-containing resin powder coating composition and an appearance of a coating film such as smoothness.

DISCLOSURE OF INVENTION

[0006] Namely the present invention relates to the electrostatic coating method of a thermosetting fluorine-containing resin powder coating composition by previously heating an article to be coated to a temperature in a range higher than a glass transition temperature of the powder coating composition and up to a temperature higher than a curing starting temperature by 10°C.

[0007] In the present invention, it is preferable that a surface of the article to be coated is a surface of metal subjected to chemical conversion treatment or a surface of metal subjected to plastic coating or coating with a paint. It is particularly preferable that the surface is subjected to coating with an aqueous paint.

BEST MODE FOR CARRYING OUT THE INVENTION

[0008] In the coating method of the present invention, known electrostatic coating equipment and electrostatic coating conditions can be employed except that the article to be coated is previously heated to a temperature in a range higher than a glass transition temperature of the thermosetting fluorine-containing resin powder coating composition and up to a temperature higher than a curing starting temperature by 10°C.

[0009] In the present invention, the glass transition temperature means a glass transition temperature of a thermosetting fluorine-containing resin to be used as a resin component of the powder coating composition and is an inherent physical property of the thermosetting fluorine-containing resin. The glass transition temperature of the thermosetting fluorine-containing resin to be used for the thermosetting fluorine-containing resin powder coating composition is a temperature higher than room temperature, usually 30° to 70°C. As the powder coating composition is heated, a curing reaction starts by a function of a curing agent contained in the composition. The curing starting temperature means a temperature where the curing reaction starts. The curing starting temperature is a temperature which is determined by a combination of the thermosetting fluorine-containing resin and the curing agent and is higher than the glass transition temperature. The curing starting temperature is usually from 120° to 150°C in case of the generally used ther-

mosetting fluorine-containing resin powder coating compositions.

[0010] When a temperature of the article to be coated is not more than a glass transition temperature of thermosetting fluorine-containing resin powder coating composition at electrostatic coating, adhesion of the powder coating composition to the article to be coated is insufficient and an adhesion efficiency is not enhanced. A lower limit of the heating temperature of the article to be coated is a temperature higher than the glass transition temperature preferably by 5°C, further preferably by 10°C.

[0011] An upper limit of the heating temperature of the article to be coated is a temperature higher than the curing starting temperature by 10°C. When higher than the upper limit temperature, the curing reaction advances quickly and the curing starts before the applied coating composition flows. Thus a surface of the obtained coating film does not become smooth. The upper limit of the heating temperature is preferably a temperature higher than the curing starting temperature by 5°C, further preferably the curing starting temperature.

[0012] A thermosetting fluorine-containing resin powder coating composition generally has a lower adhesive property to an article to be coated, particularly to a metallic substrate as compared with general-purpose resin powder coating compositions. Therefore in order to further enhance an effect of the present invention, it is preferable that a surface of the article to be coated is subjected to a specific treatment.

[0013] In case of a metallic substrate, it is preferable that a surface of the substrate to be coated is subjected to chemical conversion treatment or subjected to plastic coating or coating with a paint. It is particularly preferable that the surface is subjected to coating with an aqueous paint from the viewpoint of enhancement of adhesion of the composition to the metallic substrate and excellent environmental protection.

[0014] Examples of the preferred chemical conversion treatment are dipping in zinc phosphate, iron phosphate, chromate, chromic acid and chromate phosphate and spraying thereof.

[0015] Examples of the plastic coating treatment are coating with polyamide, polyolefin, polyester, polyvinyl chloride, polyvinylidene fluoride, and the like.

[0016] Examples of the coating with a paint are coating of an aqueous paint comprising a thermosetting acrylic resin, polyester resin, urethane resin, epoxy resin or the like in a coating thickness of 1 to 50 μm, and the like.

[0017] The thermosetting fluorine-containing resin powder coating composition to be used in the present invention is a usual thermosetting fluorine-containing resin powder coating composition basically comprising a thermosetting fluorine-containing resin powder, a curing agent and as case demands, a pigment and various additives.

[0018] The thermosetting fluorine-containing resin as a resin component is not limited particularly as far as the resin is a polymer having a fluorine-containing monomer unit and a crosslinkable reactive group as essential components.

[0019] Examples of the fluorine-containing monomer are, for instance, one or two or more of tetrafluoroethylene, chlorotrifluoroethylene, trifluoroethylene, vinylidene fluoride, hexafluoropropylene, pentafluoropropylene, perfluoro(vinyl ether), monofluoroethylene, and the like. The fluorine-containing monomer may be copolymerized with a non-fluorine-containing monomer, as case demands.

[0020] Examples of the crosslinkable reactive group are, for instance, hydroxyl group, carboxyl group, amino group, amido group, isocyanate group, halogen atoms such as bromine and iodine, and the like.

[0021] In addition to the thermosetting fluorine-containing resin mentioned above, as case demands, the above-mentioned general-purpose non-fluorine-containing thermosetting resin, for example, an epoxy resin, acrylic resin, polyester resin, or the like may be blended as a powder resin component.

[0022] As the curing agent, those which have been used for thermosetting powder coating compositions can be used. Examples thereof are, for instance, a blocked isocyanate compound, acid anhydride, polyamine compound, glycidyl compound, isocyanurate compound, polybasic acid, and the like.

[0023] Examples of the pigment are organic pigments such as condensed azo compound, isoindolenone, quinacridone, diketopyrrolopyrol, anthraquinone and dioxane; inorganic oxide pigments such as titanium oxide, iron oxide, carbon black, chromium oxide, lead chromate, white lead and molybdenum orange; metal powders such as aluminum powder and stainless steel powder; and the like.

[0024] In addition, various additives which are usually used for powder coating compositions may be optionally blended. Examples thereof are, for instance, a filler, ultraviolet ray absorber, leveling agent, flowability control agent, antioxidant, heat deterioration preventive agent, gloss control agent, electrostatic charge control agent, and the like.

[0025] Examples of the thermosetting fluorine-containing resin powder coating composition which can be used suitably in the method of the present invention are, for instance, powder coating compositions prepared by using thermosetting fluorine-containing resins which are described in JP-B-6-104792, JP-A-5-331388, Japanese Patent No. 2782726, etc. and have a relatively low glass transition temperature.

[0026] In the present invention, a method and conditions for imparting an electrostatic charge to the powder coating composition may be those usually employed. For example, for imparting an electrostatic charge at electrostatic powder coating, there are a frictional electrification method and corona electrical charging method. Since a fluorine-containing resin is easily charged with negative electricity, the corona electrical charging method is suitable. A suitable applied voltage is from 20 to 80 kV, further 40 to 60 kV. When the voltage is too high, a surface of the coating film easily

becomes rough, and when too low, an adhesion efficiency is lowered.

[0027] Then the present invention is explained by means of examples, but is not limited to them.

EXAMPLE 1

(Preparation of thermosetting fluorine-containing resin powder coating composition)

[0028] A thermosetting fluorine-containing resin powder was prepared by pulverizing a chlorotrifluoroethylene/cyclohexyl vinyl ether/isobutyl vinyl ether/hydroxybutyl vinyl ether (weight ratio: about 50/16/9/25) copolymer (hydroxyl value: 120 mgKOH/g, glass transition temperature: 45°C, weight reduction by heating: 2 % by weight or less, intrinsic viscosity (η) measured in tetrahydrofuran at 30°C: 0.21) with an impact hammer mill. After 44 parts by weight of the obtained fluorine-containing resin powder, 30 parts by weight of a filler (titanium dioxide) and 26 parts by weight of a curing agent (ADDUCT B-1530 available from Hüls Co., Ltd.) were mixed uniformly for about one minute with a dry blender (Henschel mixer available from Mitsui Kako Kikai Kabushiki Kaisha), the mixture was melt-kneaded at a temperature of from 80° to 100°C with an extrusion kneader (BUS COKNEADER PR-46 available from Bus Co., Ltd.). After cooling, a melt-kneaded product was finely pulverized with an impact hammer mill and further coarse particles were removed with a 150 mesh metal net. Thus a thermosetting fluorine-containing resin powder coating composition to be used in Examples was prepared.

[0029] With respect to the glass transition temperature of the thermosetting fluorine-containing resin, a heat balance was measured by heating 10 mg of sample from -25°C to 200°C at a temperature increasing rate of 10°C/min by using Thermal Analysis System available from Perkin Elmer Co., Ltd. and a temperature at a center point between the two variable polar points was assumed to be a glass transition temperature.

[0030] A curing starting temperature of the obtained powder coating composition was measured with a pendulum viscometer (DDV-OPA) available from Orientec Corporation. The curing starting temperature was 140°C.

[0031] Therefore when using this powder coating composition, a pre-heating temperature of an article to be coated is within a temperature range higher than 45°C and not more than 150°C.

(Electrostatic coating of powder coating composition)

[0032] A steel sheet subjected to zinc phosphate treatment in a thickness of 0.8 mm was coated with an aqueous polyurethane resin paint (VD100N available from Mitsui Toatsu Kagaku Kabushiki Kaisha) in a thickness of 10 μm to give an article to be coated. The article to be coated was heated to 100°C and immediately mounted in a booth provided with a corona discharge gun (GX3300 available from Onoda Cement Kabushiki Kaisha), followed by electrostatic coating of the above-mentioned powder coating composition at an applied voltage of 60 kV.

[0033] In that case, an adhesion efficiency (%) (= (Total amount of adhered composition (g)/Effective amount of discharged composition (g)) × 100) was 75 %.

[0034] Then the coated steel sheet was subjected to baking at 200°C for 15 minutes, and the following characteristics were evaluated. The results are shown in Table 1.

Appearance of coating film

[0035] Evaluation was made with naked eyes by the following criteria.

A: A surface of the coating film is free from unevenness and is smooth.
B: There is a gentle deformation slightly.
C: A surface of the coating film is rough (There is an unevenness apparently).

Adhesion

[0036] A cross-cut test is carried out according to JIS D 0202 8.12.

EXAMPLES 2 to 3 and COMPARATIVE EXAMPLES 1 to 2

[0037] Electrostatic coating and baking were carried out in the same manner as in Example 1 except that the following articles to be coated were used and the articles were heated to a temperature shown in Table 1. An adhesion efficiency and characteristics of the coating film were evaluated. The results are shown in Table 1.

(Articles to be coated)

Example 2: The same steel sheet as in Example 1 which is subjected to chemical conversion treatment with phosphate but not subjected to coating with a urethane resin paint

Example 3: A steel sheet which is not subjected to any treatment

Comparative Examples 1 and 2: The same steel sheet as in Example 1 which is coated with a urethane resin paint

[0038]

TABLE 1

	Heating temperature of article to be coated (°C)	Adhesion efficiency (%)	Coating thickness (μm)	Characteristics of coating film	
				Appearance (smoothness)	Adhesive property
Ex. 1	100	75	50	A	100/100
Ex. 2	100	65	53	A	100/100
Ex. 3	100	65	52	A	95/100
Com. Ex. 1	35	50	55	B	100/100
Com. Ex. 2	160	75	55	C	20/100

INDUSTRIAL APPLICABILITY

[0039] According to the coating method of the present invention, since an adhesion efficiency per one coating is enhanced, the number of coats until a desired coating thickness is obtained can be decreased and productivity is enhanced. Also since a smoothness of a surface of coating film is excellent, a coated article having good appearance can be provided.

Claims

1. A method of coating a thermosetting fluorine-containing resin powder coating composition by electrostatic coating, in which an article to be coated is previously heated to a temperature in a range higher than a glass transition temperature of the powder coating composition and up to a temperature higher than a curing starting temperature by 10°C.

2. The coating method of Claim 1, wherein a surface of the article to be coated is a surface of metal subjected to chemical conversion treatment.

3. The coating method of Claim 1, wherein a surface of the article to be coated is a surface of metal subjected to plastic coating or coating with a paint.

4. The coating method of Claim 3, wherein a surface of the article to be coated is a surface subjected to coating with an aqueous paint.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP99/05461

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl[7] B05D 3/02, B05D 1/04, B05D 7/24 301

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl[7] B05D 3/02, B05D 1/04, B05D 7/24 301

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-1999
Kokai Jitsuyo Shinan Koho 1926-1999 Jitsuyo Shinan Toroku Koho 1996-1999

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 07-148458, A (NIPPON PAINT CO., LTD.), 13 June, 1995 (13.06.95) (Family: none)	1-4
Y	JP, 06-114321, A (John Lysaght (Australia) Ltd.), 26 April, 1994 (26.04.94) & EP, 494672, A1 & US, 5281435, A	1-4
A	JP, 61-111335, A (Tokai Kogyo Kabushiki Kaisha), 29 May, 1986 (29.05.86) (Family: none)	1-4

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 December, 1999 (28.12.99)	11 January, 2000 (11.01.00)
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