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HIGHLY WEATHER-RESISTANT ELECTRODEPOSITION

COATING COMPOSITION

This invention relates to an electrodeposition coating composition, and more preferably to a highly weather-resistant electrodeposition coating composition. It may be capable of imparting an excellent weather resistance to an anodized aluminium or aluminium alloy material (hereinafter simply referred to as an aluminium material) by one electrodeposition coating alone. It further relates to a method of preparing a composition, and to coated articles.

As an example of the electrodeposition coating compositions used for coating the aluminium material, there has been known an acrylic-melamine based water-soluble or water-dispersible coating composition, for example, there is used a water-soluble or water-dispersible coating composition which is obtained by mixing melamine resin as a crosslinking agent with a water-soluble or water-dispersible resin formed by neutralizing a polycarboxylic resin obtained by copolymerization of acrylic acid or methacrylic acid with other acrylic unsaturated monomer and/or ethylenically unsaturated monomer with ammonia or organic amine. The acrylic-melamine based electrodeposition coating composition has widely been used in coating building materials such as an aluminium sash used in the general houses and high buildings due to its good corrosion resistance and weather resistance.

However, although the acrylic-melamine based electrodeposition coating composition exhibits a satisfactory weather resistance when used in the general houses, the electrodeposition coating composition is quite incapable of satisfying recent requirements for durability over a long period of time of several decades when applied to building materials for use in buildings. Accordingly, development of an improved coating composition over the conventional electrodeposition coating composition is highly demanded.

There has heretofore been known a fluorocarbon polymers based coating composition which is capable of forming a film guaranteed for 20 to 30 years as a coating composition to form a highly durable film. The fluorocarbon polymers based coating composition is to be usually coated by coating means such as air spray coating, electrostatic spray coating and roll coating, and is impossible to be uniformly coated on a substrate having complicated shapes such as the aluminium sash, resulting in that a required film thickness is not obtained uniformly, for instance, when applied to an inner portion of a concave surface and in that problems are produced in quality assurance.

Preferred embodiments of this invention provide a highly weather-resistant electrodeposition coating composition which is capable of assuring high weather resistance over several decades as recently required when

applied to building materials for use in buildings, and of being uniformly coated on substrates having complicated shapes. The present invention provides an electrodeposition coating composition obtained by:

dispersing a mixture of

(a) 20 to 90% by weight of an acrylic polycarboxylic resin prepared by copolymerizing an α,β -ethylenically unsaturated carboxylic acid with a hydroxy-group containing acrylic monomer and an ethylenically unsaturated monomer copolymerizable therewith, said resin having an acid value of from 30 to 100 and a hydroxy number of from 20 to 100,

with (b) 10 to 80% by weight of fluorocarbon polymer, which is a homopolymer or a copolymer of fluoroolefins and has a particle diameter of from 0.1 to 50 μ m and a melting point not higher than a heating temperature for curing a film formed from said electrodeposition coating composition,

in the presence of a water miscible organic solvent to form a dispersion,

followed by neutralizing the dispersion with a neutralizing agent which is ammonia or an organic amine the mixture then being water-soluble or water-dispersible.

One of the excellent features of preferred electrodeposition coating compositions of the present invention is in that the electrodeposition coating composition is capable of forming a highly weather-resistant film in one coating. The reason why such an effect is provided is that the fluorocarbon polymers used in combination with the water-soluble or water-dispersible acrylic polycarboxylic resin presents in a suspended state mostly without being dissolved in the aqueous solution, and is subjected to electrodeposition along with the acrylic polycarboxylic resin to form an electrodeposited film, which is cured at a temperature higher than the melting point of the fluorocarbon polymers, resulting in that the acrylic polycarboxylic resin and the fluorocarbon polymers melt uniformly to form a fused film in which both the acrylic polycarboxylic resin and the fluorocarbon polymers are uniformly fused. The resulting fluorocarbon polymers

containing electrodeposition coating film has not only such a high weather resistance over several decades and chemical resistance as to compete with the conventional fluorocarbon polymers containing coating film, but also is to be uniformly formed even on the substrates having complicated shapes, such as the aluminium sash.

Representative examples of the α,β -ethylenically unsaturated carboxylic acid include acrylic acid, methacrylic acid, maleic acid, and itaconic acid.

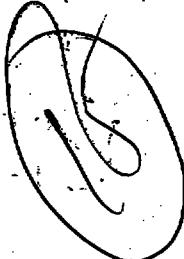
Representative examples of the acrylic monomer include acrylic ester monomers such as 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate and 3-hydroxypropyl acrylate; methacrylic ester monomers such as 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate and 3-hydroxypropyl methacrylate; and acrylic amide or methacrylic amide monomers such as N-methylolacrylamide, N-methylolmethacrylamide, and methyloldiacetone acrylamide.

Examples of the ethylenically unsaturated monomer include aromatic monomers such as styrene and vinyltoluene, carboxylic vinyl esters such as vinyl acetate and vinyl propionate, and unsaturated nitriles such as acrylonitrile and methacrylonitrile.

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It is necessary for the acid value of the acrylic polycarboxylic resin to be in the range of from 30 to 100, preferably 35 to 70, because the acrylic polycarboxylic resin should be such that the mixture of the acrylic polycarboxylic resin with the fluorocarbon polymers is made fully water-soluble or water-dispersible with ammonia or an organic amine. When the acid value of the acrylic polycarboxylic resin is lower than 30, the aqueous solution exhibits a poor dissolved state and has bad stability with time, and the film formed from a coating composition by use of such a resin exhibits poor appearance. On the other hand, when the acid value is higher than 100, weather resistance of the acrylic polycarboxylic resin itself is lowered, appearance, particularly gloss is lowered, co-electrophoretic property of the fluorocarbon polymers and an amino resin used as a crosslinking agent become poor resulting in poor film performance, and compatibility with the fluorocarbon polymers becomes bad, resulting in that cloudiness of the film is remarkably increased.



The electrodeposition coating composition of the present invention may include amino resin or block polyisocyanate which is used as the crosslinking agent. Then, the hydroxy-group containing acrylic monomer may be 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxyethyl methacrylate or 2-hydroxypropyl methacrylate. The hydroxy number of the acrylic polycarboxylic resin is in the range of from 20 to 100, preferably 30 to 80. When the hydroxy number of the resin is lower than 20, physical properties of the film formed therefrom are poor. On the other hand, when higher than 100, compatibility with the fluorocarbon polymers becomes bad, resulting in that cloudiness of the film is remarkably increased.

The fluorocarbon polymers used in the present invention may be homopolymers or copolymers of fluoroolefins such as tetrafluoroethylene, hexafluoropropene, chlorotrifluoroethylene, vinylidene fluoride or vinyl fluoride; copolymers of these fluoroolefins with olefins such as ethylene and propylene and/or fluorovinyl ethers, provided that the copolymer contains at least 50% by weight of fluoroolefin; and the like, and has melting point not

higher than a heating temperature for curing a film formed from the electrodeposition coating composition in the present invention. Specific examples of the fluorocarbon polymers include polytetrafluoroethylene, polychlorotrifluoroethylene, polyvinylidene fluoride, polyvinyl fluoride, tetrafluoroethylene-hexafluoropropene copolymer, ethylene-chlorotrifluoroethylene copolymer, tetrafluoroethylene-fluorovinyl ether copolymer, ethylene-tetrafluoroethylene-fluorovinyl ether terpolymer, and the like, polyvinylidene fluoride being preferred.

It is not necessary for the fluorocarbon polymers to be uniformly dissolved in the aqueous system, so long as the fluorocarbon polymers is capable of forming a suspension therein. The particle diameter of the fluorocarbon polymers used is in the range of from 0.1 to 50 millimicron (μ m). A dispersion of the fluorocarbon polymers, which is prepared by normal emulsion polymerization, contains the fluorocarbon polymers having a particle diameter of from about 0.1 to 3.0 micrometer, and may be preferably used in the coating composition of the present invention as it is.

The melting point of the fluorocarbon polymers used in the present invention is preferably not higher than a temperature for curing a film formed from the electrodeposition coating composition in the present invention, preferably not higher than 200°C, whereby the acrylic polycarboxylic resin-fluorocarbon polymers film

is formed in such a state that while the film of the coating composition of the present invention is heated for curing, the fluorocarbon polymers is partly melted or softened to be uniformly distributed into the film. When the melting point of the fluorocarbon polymers is higher than the heating temperature for curing, any film with uniform distribution is not obtained to form a film in which the fluorocarbon polymers is isolated, resulting in that good durability of the fluorocarbon polymers is not fully exhibited.

The mixing ratio of the acrylic polycarboxylic resin to the fluorocarbon polymers is such that the former is in the range of from 20 to 90% by weight, preferably 30 to 80% by weight, while the latter is in the range of from 10 to 80% by weight, preferably 20 to 70% by weight. When the amount to be used of the acrylic polycarboxylic resin is less than 20% by weight, or the amount to be used of the fluorocarbon polymers is more than 80% by weight, preparation of uniform and stable electrodeposition bath is made difficult.

On the other hand, when the amount to be used of the acrylic polycarboxylic resin is more than 90% by weight, or the amount to be used of the fluorocarbon polymers is less than 10% by weight, the highly weather-resistant electrodeposition coating composition according to the present invention is not obtained.

As required, conventionally known amino resin

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and block polyisocyanate may be used as the crosslinking agent in the electrodeposition coating composition of the present invention. Adducts with formaldehyde of melamine, urea, benzoguanamine, acetoguanamine or mixtures thereof, and alcohol etherified compounds thereof may be used as the amino resin, which is not required to be water-soluble.

The block polyisocyanate may be prepared by reacting polyisocyanate compound with a blocking agent such as alcohol and phenol. Examples of the polyisocyanate compound include tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, xylylene diisocyanate, methaxylylene diisocyanate, hexamethylene diisocyanate, lysine diisocyanate, 4,4'-methylene bis (cyclohexylisocyanate), methylcyclohexane 2,4(2,6) diisocyanate, 1,3-(isocyanate methyl) cyclohexane, isophorone diisocyanate, trimethylhexamethylene diisocyanate, and the like.

The amino resin and the block polyisocyanate may be used alone or in combination. They may be used in an amount not more than 10% by weight of the electrodeposition coating composition of the present invention.

Examples of ammonia and the organic amine used as the neutralizing agent for making water-soluble in the present invention include ammonia, dimethylamine, trimethylamine, diethylamine, triethylamine, diisopropylamine, butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, triisopropanolamine, N-methyl-

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ethanolamine, N-aminoethylethanolamine, N-methyl-diethanolamine and polyglycolamine. These neutralizing agents are used in an amount of from 0.3 to 1.2 equivalents with respect to carboxyl group in the acrylic polycarboxylic resin.

The electrodeposition coating composition of the present invention is liable to form a film with cloudiness because of containing the fluorocarbon polymers originally having bad compatibility as a binder component with the result that the cloudiness gives no adverse influence on the weather resistance and chemical resistance of the film. However, when a transparent film free from cloudiness is required, a transparent film may be formed by maintaining the acid value and the hydroxyl number of the acrylic polycarboxylic resin as low as possible within the aforesaid range and by lowering the value of the solubility parameter thereof to improve compatibility with the fluorocarbon polymers.

Water miscible organic solvents are used in the electrodeposition coating composition of the present invention in order to aid to make the acrylic polycarboxylic resin water-soluble or dispersible. Examples of the water miscible organic solvent include alcohols such as methyl alcohol, ethyl alcohol, isopropyl alcohol and butyl alcohol; Cellosolve* type solvents such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether and ethylene glycol monobutyl ether; propylene glycol ethers, ethylene glycol

ethers, and the like.

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As required, conventionally used additives such as surface active agents, pigments and crosslinking accelerator may be incorporated in the electrodeposition coating composition.

The conventional electrodeposition process may be applied to the coating composition of the present invention, and the electrodeposition may be carried out, for example, under the conditions of a bath temperature of from 15° to 35°C, a bath concentration of from 4 to 15% by weight and a coating voltage of from 80 to 350V.

Metals such as iron, copper and aluminium may be used as the substrate to be coated, and the aluminium materials such as plates, bars, tubes or other articles with complicated shapes of the anodized aluminium, to which the electrodeposition coating composition of the present invention is particularly effective, are preferred.

The present invention will be explained more in detail by the following Examples and Comparative Examples, in which parts and % are all by weight.

Preparation Examples of Acrylic Polycarboxylic Resins:

Preparation Example 1

Fifty parts of butylcellosolve* is charged into a reactor and heated to 90°C. A mixture of 45 parts of methylmethacrylate, 37 parts of n-butylacrylate, 10 parts of hydroxyethylmethacrylate, 8 parts of acrylic acid and 2 (two) parts of azobisisobutyronitrile is dropped thereinto

over 3 hours. After the completion of the dropping procedure, heating with agitation is further continued for polymerization. A solids concentration of an acrylic polycarboxylic resin solution thus obtained is 67%, and an acid value of the resin is 65.

Preparation Example 2

An acrylic polycarboxylic resin solution is prepared in the same manner as in Preparation Example 1 except that 42 parts of n-butylacrylate and 3 parts of acrylic acid are used. A solids concentration of an acrylic polycarboxylic resin solution obtained is 67%, and an acid value of the resin is 23.

Preparation Example 3

An acrylic polycarboxylic resin solution is prepared in the same manner as in Preparation Example 1 except that 32 parts of n-butylacrylate and 13 parts of acrylic acid are used. A solids concentration of the acrylic polycarboxylic resin solution is 67%, and an acid value of the resin is 105.

Example 1

To a ball mill are charged 15 parts of the acrylic polycarboxylic resin solution in Preparation Example 1, 10 parts of diethylene glycol monobutyl ether, 10 parts of isopropyl alcohol and 40 parts of Kynar* V500 (vinylidene polyfluoride resin, Trade Name, marketed by Pennwalt Corp., U.S.A.) to be subjected to dispersion for 20 hours. To a dispersion thus obtained are added 1.0 part of

triethylamine and 424 parts of deionized water to be dispersed with agitation and to obtain a water-soluble coating composition having a solids concentration of 10%.

Examples 2-5 and Comparative Examples 1-3

Water-soluble coating compositions having a solids concentration of 10% are prepared in the same manner as in Example 1 according to formulations shown in Table-1.

Anodized aluminium plates (anodized film thickness: 10 μ) are immersed in water-soluble coating composition bathes obtained in the above Examples and Comparative Examples, electrodeposition coating is carried out for 3 minutes under the conditions shown in Table-1, the anodized aluminium plates being used as the anode. Coated anodized aluminium plates obtained and having a film thickness of from 10 to 15 μ are washed with water and cured at 200°C for 30 minutes. Results of film performance tests are shown in Table-1.

Table-1

	Example					Comparative Example		
	1	2	3	4	5	1	2	3
Resin in Preparation Example 1	15	30	52.5	30	30	67.5		
Resin in Preparation Example 2							30	
Resin in Preparation Example 3								30
Kynar V500 #1	40	30	15	30	30	5	30	30
Diethylene glycol monobutyl ether	10	7.5	3.75	7.5	7.5		7.5	7.5
Isopropyl alcohol	10	7.5	3.75	7.5	7.5		7.5	7.5
Triethyl amine	1.0	2.0	3.5	2.0	2.0	4.5	0.7	3.2
Water	424	423	421.5	421	421	424.3	424.3	421.8
Melamine resin #2				2				5
Block isocyanate #3					2			
Coating voltage (V)	60	100	150	80	80	180	100	150
States of film (Determination by the naked eye)	delustered, good	delustered, good	half-delustered, good	delustered, good	delustered, good	delustered, lustered, good	unevenness of deposition	increased cloudiness
Adhesion properties #4	Good	good	good	good	good	good	good	good
Gloss retention (%) #5	85	65	60	70	73	10 >	-	65

*1: Polyvinylidene fluoride resin

*2: Nikalac MX-40 (partially butoxyfied methyl-aminotriazine, marketed by Sanwa Chemicals Co., Ltd.)

*3: Butylcellosolve blocked compound of isophorone diisocyanate

*4: Adhesion test with squares

*5: Gloss retention after 5,000 hours exposure to Sunshine Weather-o-meter



CLAIMS:

1. An electrodeposition coating composition obtained by:

dispersing a mixture of

(a) 20 to 90% by weight of an acrylic polycarboxylic resin prepared by copolymerizing an α,β -ethylenically unsaturated carboxylic acid with a hydroxy-group containing acrylic monomer and an ethylenically unsaturated monomer copolymerizable therewith, said resin having an acid value of from 30 to 100 and a hydroxy number of from 20 to 100,

with (b) 10 to 80% by weight of fluorocarbon polymer, which is a homopolymer or a copolymer of fluoroolefins and has a particle diameter of from 0.1 to 50 μ m and a melting point not higher than a heating temperature for curing a film formed from said electrodeposition coating composition,

in the presence of a water miscible organic solvent to form a dispersion,

followed by neutralizing the dispersion with a neutralizing agent which is ammonia or an organic amine the mixture then being water-soluble or water-dispersible.

2. A coating composition according to claim 1 wherein said water-miscible organic solvent is selected from alcohols and Cellosolve-type solvents.

3. A coating composition according to claim 1 or 2 incorporating amino resin or block polyisocyanate as crosslinking agent.

4. A coating composition according to any preceding claim



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wherein the melting point of the fluorocarbon polymer is not higher than 200°C.

5. A coating composition according to any one of the preceding claims wherein the fluorocarbon polymer is polyvinylidene fluoride.

6. A coating composition according to any one of the preceding claims, wherein said acrylic monomer is selected from 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxyethyl methacrylate and 2-hydroxypropyl methacrylate.

7. A coating composition according to any one of the preceding claims, wherein in said coating composition said organic solvent is selected from methyl alcohol, ethyl alcohol, isopropyl alcohol, butyl alcohol, ethylene glycol monomethylether, ethylene glycol monoethylether, ethylene glycol monobutylether, propylene glycol ethers, and ethylene glycol ethers.

8. An electrodeposition coating composition substantially as described herein and exemplified in any of examples 1 to 5.

9. An article having a portion of an aluminium material to which a coating composition according to any preceding claim has been applied.

10. An article according to claim 7, wherein said aluminium material is an anodized aluminium building material.

11. A method of preparing a coating composition comprising dispersing a mixture of



(a) 20 to 90% by weight of an acrylic polycarboxylic resin prepared by copolymerizing an α,β -ethylenically unsaturated carboxylic acid with a hydroxy-group containing acrylic monomer and an ethylenically unsaturated monomer copolymerizable therewith, said resin having an acid value of from 30 to 100 and a hydroxy number of from 20 to 100,

with (b) 10 to 80% by weight of fluorocarbon polymer, which is a homopolymer or a copolymer of fluoroolefins and has a particle diameter of from 0.1 to 50 μ and a melting point not higher than a heating temperature for curing a film formed from said electrodeposition coating composition,

in the presence of a water miscible organic solvent to form a dispersion,

followed by neutralizing the dispersion with a neutralizing agent which is ammonia or an organic amine the mixture then being water-soluble or water-dispersible.

12. A method according to claim 11 for preparing a coating composition according to any of claims 1 to 8.
