

DESCRIPTION

CATIONIC ELECTRODEPOSITION COATING COMPOSITION FOR ELECTRONIC PARTS

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a cationic electrodeposition coating composition for electronic parts, and in particular to a lead-free type cationic electrodeposition coating composition for electronic parts which substantially does not contain lead and tin.

Description of Background Art

In order to protect metallic materials from corrosion and to keep beautiful appearance over their service life, the metallic materials are generally subjected to surface coating. Electrodeposition coating is often used for undercoating an object which requires high rust resistance because electrodeposition coating makes it possible to coat details of an object to be coated having a complicated shape, automatically and continuously. In recent years, electronic parts such as cases for a computer hard disk and components for a motor are also subjected to the electrodeposition coating.

[0003] Electrodeposition coating generally includes an electrodeposition process and a curing process. In the electrodeposition process, an object to be coated is dipped into a bath of an electrodeposition coating composition, the object is used as a cathode, and a voltage is applied between the cathode and an anode, thereby a solid of the coating composition is deposited in the form of a coated film on a surface of the object to be coated. In the curing

process, the solid deposited on the surface of the object to be coated is baked at 120 to 260°C, thereby it is cured.

The electrodeposition coating composition is an emulsion in which an ionized binder component, a pigment component and the like are dispersed in an aqueous medium. The object to be coated is not particularly limited insofar as it has conductivity, and examples of which include iron plates, steel plates and aluminum plates, the sheets of which surface is treated, and molded products of the plates.

The binder component is generally a thermocurable resin composition. The curing system composed of an amine modified epoxy resin and a blocked isocyanate curing agent is widely used as a binder for an electrodeposition coating composition since it is superior in adhesiveness, corrosion resistance, throwing power and the like.

The pigment component is a component that generally gives color and hiding power to coated film. Furthermore, in an application where excellent corrosion proof property is required, a corrosion proof pigment may be added as the pigment component. As the corrosion proof pigment, organic lead compounds have been conventionally used.

Lead ion originating from organic lead compounds functions as a curing catalysis for the curing system composed of an epoxy resin and a blocked isocyanate, and it reduces curing temperature and promotes curing. As a result of this, durability, corrosion proof property, rust proof property and the like of the coated film are improved, and thus organic lead compounds are useful as the rust proof pigment.

However, organic lead compounds are toxic, and it is not preferred

that they spread around the environment with being included in coated film of products. Therefore, from the viewpoint of safety to human bodies and natural environments, it is preferred that the organic lead compounds are not employed. Organic tin compounds are also toxic, and may cause environmental problems as described above. Further if an electrodeposition coating composition containing the organic tin compounds is applied to electronic parts, an electronic device having the parts may become defective in quality.

This is because when internal temperature of the electronic device increases and components remaining in the coated film vaporize, the vaporized gas may exert adverse effects on electronic circuits of the electronic device. Therefore, it is desired to reduce in quantity a minor volatile component that will gradually vaporize after the coated film is cured, so-called outgas remaining in the cured coated film.

SUMMARY OF THE INVENTION

The present invention is intended to solve the above-mentioned conventional problems and it is an object of the present invention to provide a lead-free type cationic electrodeposition coating composition for electronic parts which does not contain lead and tin that is likely to exert adverse effects on the environment, and shows excellent curability, while provides cured coated film excellent in durability, corrosion proof property and rust proof property, and reduced in outgas content.

The present invention provides a cationic electrodeposition coating composition for electronic parts which contains an amine modified

epoxy resin and a blocked isocyanate curing agent as a binder component, wherein

the amine modified epoxy resin is an amine modified polyphenolpolyglycidyl ether type epoxy resin,

the blocked isocyanate curing agent is a mixture of blocked isocyanate that is obtained by blocking alicyclic isocyanates and blocked isocyanate that is obtained by blocking isocyanates having aromatic ring,

the coating composition substantially does not contain lead and tin.

In the above, “substantially does not contain lead” means that lead is not contained in such an amount that will exert adverse effects on the environment. More specifically, it means that the concentration of lead ion in the cationic electrodeposition coating composition does not exceed 50 ppm, preferably 10 ppm. Likewise, “substantially does not contain tin” means that tin is not contained in an amount that will exert adverse effects on the environment and the quality of the electronic parts. To be more specific, it means that the concentration of tin ion in the cationic electrodeposition coating composition does not exceed 1 ppm.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

A cationic electrodeposition coating composition is an emulsion wherein an ionized binder component, a pigment component and the like are neutralized by a neutralizer and dispersed in an aqueous medium.

Binder component

The binder component of the cationic electrodeposition coating composition is generally a thermocurable resin composition, and contains a

main agent and a curing agent. The cationic electrodeposition composition according to the present invention contains a cationized resin as the main agent and blocked isocyanate as the curing agent.

It is necessary that the cationized resin is an aqueous resin that exhibits water dispersibility. Examples of the cationized resin include amine modified epoxy resins, amine modified polyurethane polyol resins, amine modified polybutadiene resins, amine modified acrylic resins, or a sulfonium group containing resins and phosphonium group containing resins and the like. A preferred cationized resin is an amine modified epoxy resin.

Typically, an amine modified epoxy resin is produced by ring-opening all the epoxy groups of an epoxy resin by amine, or ring-opening part of the epoxy groups of an epoxy resin by other active hydrogen compound, while ring-opening the remaining epoxy groups by amine.

The epoxy resin used herein has a molecular weight of generally 600 to 4000, preferably 700 to 3000 and an epoxy equivalent of 300 to 2000, preferably 350 to 1500. Preferably, polyphenol polyglycidyl ether type epoxy resins such as bisphenol A, bisphenol F, bisphenol S, phenol novolak, and cresol novolak are used.

Oxazolidone ring containing epoxy resins as described by paragraph "0004", chemical formula 3 in Japanese Patent Laid-Open Publication No. H5(1993)-306327 may be used as the epoxy resin. This is because coated film having excellent heat resistance and corrosion resistance can be obtained.

For introducing an oxazolidone ring into an epoxy resin, block polyisocyanate blocked with lower alcohol such as methanol and polyepoxide

are heated and kept warm in the presence of a basic catalyst, and by-produced lower alcohol is distilled off, whereby an oxazolidone ring containing epoxy resin can be obtained.

When an oxazolidone ring containing epoxy resin is used, coated film having excellent heat resistance and corrosion resistance, as well as having excellent impact resistance can be obtained. Concrete examples and production methods of the oxazolidone ring containing epoxy resin are described in the paragraphs "0012" to "0047" of Japanese Patent Application No. H10(1998)-305294.

These epoxy resins may be modified by suitable resins such as polyester polyol, polyether polyol and monofunctional alkyl phenol. Examples of resins to be used for the modification include polycaprolactondiol and ethylene oxide addition polymer.

Also, chain length of the epoxy resin may be elongated by utilizing reaction between epoxy groups and diol or dicarboxylic acid. Examples of the diol include alkylene diols such as ethylene glycol, 1,2-propylene glycol, 1,3-propanediol, 1,4-butanediol and 1,6-hexanediol; alicyclic diols such as 1,2-cyclohexanediol and 1,4-cyclohexanediol; aromatic diols such as bisphenol A, bisphenol F, resorcinol, hydroquinone and the like. Examples of the dicarboxylic acid include aliphatic dicarboxylic acids such as succinic acid, adipic acid, azelaic acid, dodecanoic diacid, dimeric acid, C₁₈ to C₂₀ long-chain aliphatic dicarboxylic acids and end carboxyl group-modified butadiene-acrylonitrile copolymers, or aromatic dicarboxylic acids such as phthalic acid, isophthalic acid and terephthalic acid.

Amines used for opening the epoxy groups are generally primary

amines, secondary amines or tertiary amines. Examples of which include butylamine, octylamine, diethylamine, dibutylamine, methylbutylamine, monoethanolamine, diethanolamine, N-methylethanolamine, triethylamine hydrochloride, N,N-dimethylethanolamine acetate, and secondary amines obtainable by blocking primary amines such as ketimines of aminoethylethanolamine and diketimines of diethylenetriamine. A plurality of amines may be used in combination.

Primary amines are 2 equivalents, and they act as a chain extending agent of an epoxy resin and make the epoxy resin high molecular weight. These amines to be reacted with epoxy groups are preferably used so as to be substantially equivalent to the epoxy groups of the epoxy resin.

Number-average molecular weight of an amine modified epoxy resin determined by the GPC analysis is preferably 600 to 4000. If the number-average molecular weight is less than 600, film forming property becomes insufficient, whereas if it is more than 4000, it becomes difficult to emulsify or to solubilize in water.

Blocked isocyanate curing agent

A blocked isocyanate curing agent used in the cationic electrodeposition coating composition of the present invention is a mixture of blocked isocyanate that is obtained by blocking alicyclic isocyanates and blocked isocyanate that is obtained by blocking isocyanates having aromatic ring. This blocked isocyanate curing agent is preferably a mixture of blocked isocyanate that is obtained by blocking alicyclic isocyanates with oxime and blocked isocyanate that is obtained by blocking isocyanates having aromatic ring with lower alcohol.

For example, the blocked isocyanate curing agent may be a mixture of blocked isocyanate that is obtained by blocking dicyclohexylmethane 4,4'-diisocyanate, norbornane diisocyanate or isophorone diisocyanate with oximes; and blocked isocyanate that is obtained by blocking isocyanates which are adducts of aromatic diisocyanate and polyalcohol with lower alcohol having 1 to 4 carbon atom(s).

In the alicyclic isocyanates blocked with oximes, dissociation of the block agent proceeds at relatively low temperature, and crosslinking reaction with the main resin completes in a relatively short period, and relatively hard coated film is provided. However, when only the alicyclic isocyanates are used, crosslinking density of the coated film is low and the cured coated film tends to be too brittle, and hence durability of the coated film may become poor.

On the other hand, as for the isocyanates having aromatic ring, the number of the functional groups of the curing agent is high, the crosslinking density of polymer backbone, and stiffness and strength of the coated film are improved. However, when only the blocked isocyanate that is obtained by blocking isocyanates having aromatic ring with lower alcohol is used, temperature for curing the coated film completely tends to be too high.

In the present invention, coated film having high static T_g is provided by using as a curing agent, a mixture of the isocyanate that is obtained by blocking alicyclic isocyanates with oximes and the isocyanate that is obtained by blocking isocyanates having aromatic ring with lower alcohol. Furthermore, the curing reaction maybe completed at relatively

low temperature in this coating composition, weight loss by baking is reduced, and the coated film which generates less amount of outgas is provided.

As the isocyanates having aromatic ring, an adduct of aromatic diisocyanate and polyalcohol is preferred. This is because high Tg coated film required as electrodeposition coated film for electronic parts can be easily obtained for structural reasons.

In such a case, as the aromatic diisocyanate, aromatic compounds such as m-phenylene diisocyanate, p-phenylene diisocyanate, 4,4'-diphenyl diisocyanate, 1,5-naphthalene diisocyanate, 1,4-naphthalene diisocyanate; 4,4'-diphenylmethane diisocyanate, 2,4-or 2,6-toluene diisocyanate or mixtures thereof, aliphatic-aromatic compounds such as 4,4'-toluidine diisocyanate and 1,4-xylene diisocyanate; nuclear substituted aromatic compounds such as dianisidine isocyanate, 4,4-diphenylether diisocyanate, chlorodiphenyl diisocyanate and the like may be used.

Particularly preferred diisocyanates are toluene diisocyanate, diphenylmethane diisocyanate and their hydrides and polymers. These diisocyanates have excellent reactivity and can be easily modified in various ways, and hence high Tg coated film required as coated film for electronic parts can be easily obtained.

As a block agent of aromatic isocyanates, lower alcohol having up to 5 carbon atoms is preferably used. Lower alcohol has low boiling point, and will volatilize almost completely at the time of baking and no longer remain in cured coated film. As a result of this, lower alcohol will not be released from the cured coated film in the form of outgas.

Concrete examples of the lower alcohol include methanol, ethanol, propanol, butanol and the like. Preferred lower alcohol is methanol, ethanol and a mixture of methanol and ethanol. These have relatively low boiling points among lower alcohol, and will almost not remain in coated film after baking. Moreover, since these have small molecular weight, the weight of dissociating component per equivalent of an isocyanate group becomes small.

On the other hand, concrete examples of alicyclic isocyanates in an isocyanate that is obtained by blocking alicyclic isocyanates with oxime include dicyclohexylmethane 4,4'-diisocyanate, norbornane diisocyanate, 1,3-cyclopentane diisocyanate, 1,4-cyclohexane diisocyanate, 1,2-cyclohexane diisocyanate, isophorone diisocyanate and the like. Particularly preferred alicyclic isocyanates is isophorone diisocyanate.

As a block agent for alicyclic isocyanates, oxime is preferably used. This is because oxime has low boiling point and hence will almost not remain in coated film after baking.

Concrete examples of oxime include formaldoxime, acetaldoxime, acetoxime, methyl ethyl ketoxime, diacetyl monoxime, cyclohexane oxime and the like. Particularly preferred oxime is methyl ethyl ketoxime. Accordingly, particularly preferred isocyanate that is obtained by blocking alicyclic isocyanates is isophorone diisocyanate blocked with methyl ethyl ketoxime.

Mixing ratio of alicyclic isocyanates blocked with oxime and aromatic isocyanates blocked with lower alcohol is preferably 50/50 to 95/5 by solid weight. If the mixing ratio is less than 50/50, the curing

temperature tends to rise too high, whereas if the mixing ratio is more than 95/5, the coated film tends to be brittle to deteriorate durability.

A blocked isocyanate curing agent is generally prepared by causing the isocyanates and the block agent to react.

The reaction is conducted by mixing them and heating to a predetermined temperature. One may be added to the other that is being heated. Generally, the block agent is added dropwise to the isocyanates that is being heated. Reaction temperature is usually 50 to 70°C. As for mixing ratio of the isocyanates and the block agent, it is necessary that the block agent is excessive in the ratio of not less than 1/1 by equivalent, however, from the view point of the reactivity, the ratio is favorably not less than 1/1.1.

If the amount of the block agent is too small, it is not preferable because isocyanate groups will remain in the system and pose the problem of toxicity and possibility of side reaction with active points in the main resin when used as a coating composition. Furthermore, a block agent contained excessively will act as a solvent, and volatile substances will increase.

As a catalyst for promoting the reaction, tertiary amine, preferably tertiary amine having volatility is used. This is because tertiary amine will not exert adverse effects on the environment in comparison with organic tin, and if it has volatility, it will not remain in coated film because it will vaporize completely during the curing process and hence it will not spread around the environment with being included in coated film of products.

The tertiary amine may be added in any point of time in the

reaction course. For example, when a block agent is added to heated isocyanates, the tertiary amine is added together with the block agent. It may be added at once, or in plural times, or may be added dropwise little by little.

An end point of the reaction is determined by measuring the amount of isocyanate groups remaining in the reaction mixture. Measurement is carried out by back titration of isocyanate that has been inactivated by excess amine with the use of hydrochloric acid aqueous solution. Then, the reaction is terminated when the ratio of remaining isocyanate groups is less than 1%.

Adding amount of tertiary amine is 0.01 to 5% by weight, preferably 0.1 to 1% by weight with respect to isocyanates. If the adding amount is less than 0.01% by weight, catalytic effect will not appear, and if the adding amount is more than 5% by weight, vaporizing substances will increase.

Boiling point of the tertiary amine is 50 to 300°C, preferably 80 to 220°C. If the boiling point is less than 50°C, volatility is so high that it will vaporize during the reaction course, and thus the effect as a catalyst is insufficient.

Concrete examples of tertiary amine include aliphatic tertiary amines such as N-methyldiethylamine, N,N-dimethylisopropylamine, tri-n-ethylamine, tri-n-butylamine, tri-n-hexylamine, N,N-diethylcyclohexylamine, N,N-diethylbutylamine, N,N-dimethyloctylamine and N,N-dimethylpropargylamine; alicyclic tertiary amines such as 1,4-diazabicyclo[2.2.2]octane, 1,8-diazabicyclo[5.4.0]undecene and 1,5-

diazabicyclo[4.3.0]nondecene; aromatic tertiary amines such as N,N-dimethylbenzylamine; substituted anilines such as N,N-dimethylaniline and N,N-diethylaniline; substituted toluidines such as N,N-dimethyltoluidine and the like. Particularly preferred tertiary amines are aliphatic tertiary amines.

In order to adjust curability of the binder component, a usual urethane cleavage catalyst may be contained in the cationic electrodeposition coating composition according to the present invention. However, in coating electronic parts, it is preferred not to use tin compounds such as dibutyltin dilaurate and dibutyltin oxide which easily vaporize from the coated film in order to prevent quality of the electronic parts from being deteriorated. Furthermore, it is preferred not to use such a compound that will remain in cured coated film after curing process and gradually vaporize since such a compound will increase the amount of outgas of the cured coated film.

Preferably, the cationic electrodeposition coating composition for electronic parts according to the present invention contains an organic zinc compound. Zinc ion functions as a curing catalyst for the curing system consisting of an epoxy resin and a blocked isocyanate, and will not vaporize from the coated film to deteriorate quality of the electronic parts as is the case of organic tin compounds remaining in the cured coated film.

The organic zinc compound may be introduced as a part of neutralizer or as pigment into the coating composition. The neutralizer means a component which binds to a cationic group included in the cationized resin to form a salt, thereby making the cationized resin

dispersible in an aqueous medium.

As the part of the neutralizer, zinc acetate, zinc lactate and the like can be used. As the pigment, zinc molybdate, zinc cyanide, zinc oxide, zinc phosphate, zinc phosphomolybdate and the like can be contained.

In connection with this, the amount of zinc contained in the entire coating composition is preferably in the concentration of not less than 50 ppm. The amount of zinc herein means an amount of zinc in terms of metal ion rather than compound. If the concentration of zinc ion in the coating composition is less than 50 ppm, curability of the coated film maybe deteriorated.

Furthermore, for the cationic electrodeposition coating composition for electronic parts according to the present invention, other neutralizer and pigment which are commonly used may be used together. Examples of such neutralizer to be used include inorganic acids and organic acids such as hydrochloric acid, formic acid, acetic acid and lactic acid. Examples of such pigment include coloring pigments such as titanium white, carbon black and red iron oxide; extender pigments such as kaolin, talc, aluminum silicate, calcium carbonate, mica, clay and silica; rust proof pigments such as iron phosphate, aluminum phosphate, calcium phosphate, aluminum tripolyphosphate, aluminum molybdate, calcium molybdate and aluminum phosphomolybdate and the like.

When pigment is used as a component of the electrodeposition coating composition, the pigment is generally dispersed in an aqueous medium in high concentration to render it a paste state. This is because since the pigment is in powder state, it is difficult to disperse the pigment

uniformly in low concentration which is used for the electrodeposition coating composition, by a single process. Generally, such a paste is referred to as a pigment dispersed paste.

A pigment dispersed paste is prepared by dispersing pigment in an aqueous medium together with a pigment dispersing resin. As the pigment dispersing resin, cationic or nonionic surfactants of low molecular weight, cationic polymers such as modified epoxy resins having a quaternary ammonium group and/or a tertiary sulfonium group or the like are generally used.

After mixing these components, the mixture is dispersed until a predetermined uniform particle size of the pigment is reached to obtain a pigment dispersed paste. For dispersing pigment, a dispersing apparatus is usually used. For example, a ball mill, a sand grind mill or the like are used. Particle size of the pigment included in the pigment dispersed paste is usually not more than 15 μm .

The cationic electrodeposition coating composition according to the present invention may contain a component which commonly contained in a cationic electrodeposition coating composition in an amount which is commonly used, in addition to the above-mentioned binder component, pigment component, neutralizer and the like. As such a component, gel microparticles, viscosity adjusting agents, surfactants, antioxidants, ultraviolet absorbers and the like can be recited, for example.

The cationic electrodeposition coating composition according to the present invention is prepared by dispersing the aforementioned binder component containing a blocked isocyanate curing agent and an amine

modified epoxy resin and the like, the pigment component and other components usually contained in a cationic electrodeposition coating composition in an aqueous medium containing a neutralizer. Dispersion of these components can be carried out in a usual manner.

Besides water, other various kinds of organic solvents may be used in the aqueous medium, for example, for dissolving the resin and adjusting the viscosity. Examples of usable solvents include hydrocarbons (for example, xylene or toluene), alcohols (for example, methyl alcohol, n-butyl alcohol, isopropyl alcohol, 2-ethylhexyl alcohol, ethylene glycol and propylene glycol), ethers (for example, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol monoethyl ether, propylene glycol monoethyl ether, 3-methyl-3-methoxy butanol, diethylene glycol monoethyl ether and diethylene glycol monobutyl ether), ketons (for example, methylisobutylketone, cyclohexanone, isophorone and acetylacetone), esters (for example, ethylene glycol monoethyl ether acetate and ethylene glycol monobutyl ether acetate) and mixtures thereof. The using amount of these solvents is about 0.01 to 25% by weight, preferably 0.05 to 15% by weight with respect to the entire coating composition.

The amount of the curing agent is adjusted so that it reacts with active hydrogen containing functional groups such as primary, secondary or/and tertiary amino groups, hydroxyl groups and the like in the cationized resin at the time of curing, thereby presenting favorable cured coated film. Blending ratio of the blocked isocyanate curing agent and the amine modified epoxy resin is 10/90 to 50/50, preferably 20/80 to 40/60 by solid weight. If the blending ratio is less than 10/90, curability of the coated film

is insufficient, whereas if the blending ratio exceeds 50/50, physical properties of the coated film are insufficient due to short of the resin backbone component.

The amount of the neutralizer is generally such that it neutralizes at least 20%, preferably 30 to 60% of amino groups in the amine modified epoxy resin.

When a pigment dispersed paste is blended into the cationic electrodeposition coating composition, the blending amount of the pigment dispersed paste is preferably such that the pigment does not exceed 50% by solid weight in the cationic electrodeposition coating composition.

In the case of performing electrodeposition coating using the cationic electrodeposition coating composition according to the present invention, cases of a computer hard disk, parts of a magnetic recording apparatus such as motor parts manufactured by aluminum die-casting or magnesium die-casting are preferably used as an object to be coated. This is because coated film obtained by using the present cationic electrodeposition coating composition have excellent rust proof property, and emit reduced amount of outgas which may cause failures (memory breakage and the like) of electronic parts.

The cationic electrodeposition coating composition for electronic parts according to the present invention does not contain organic lead and organic tin. Therefore, there is reduced possibility of exerting adverse effects on the environment. Furthermore, it has excellent curability, while realizing excellent corrosion proof property of the cured coated film and reduction in amount of outgas of the cured coated film.

The present invention will be explained more concretely by way of the following examples, however the present invention is not limited to these examples. All parts and percents therein are by weight unless otherwise indicated.

Production example 1

Synthesis of amine modified epoxy resin

950 parts of a bisphenol A epoxy resin (Epo-Tohto YD-014 available from Tohto Kasei Co.) having an epoxy equivalent weight of 950 was put into a reaction vessel equipped with a stirrer, a nitrogen introducing tube, a condenser and a thermometer together with 237.5 parts of methylisobutylketone, and heated to 100°C so as to cause them to completely dissolve. Then, 60 parts of n-methylethanolamine and 73 parts of 73% methyl isobutyl ketone solution of methyl isobutyl diketimine of diethylenetriamine was added and the resultant mixture was kept at 120°C for one hour to obtain an amine modified epoxy resin.

Production example 2

Synthesis of blocked isocyanate curing agent

In a reaction vessel equipped with a stirrer, a thermometer, a condenser and a nitrogen introducing tube was put 222 parts of isophorone diisocyanate and diluted with 56 parts of methyl isobutyl ketone. After raising the temperature to 50°C, 174 parts of methyl ethyl ketoxime was added so that the temperature did not exceed 70°C. The mixture was held at 70°C for 1 hour until absorption of isocyanate groups substantially disappeared as observed by infrared absorption spectrum, and then the mixture was diluted with 43 parts of n-butanol.

Production example 3

Synthesis of blocked isocyanate curing agent

1250 parts of 4,4'-diphenylmethane diisocyanate, 685 parts of methyl isobutyl ketone and 6.25 parts of tributylamine were placed in a reaction vessel, and heated to 60°C. To this reaction mixture 120 parts of methanol and 173 parts of ethanol were added dropwise at a constant rate over 3 hours. Then, 112.5 parts of trimethylolpropane and 237.5 parts of methyl isobutyl ketone were added and the temperature was raised to 110°C, to allow them to react for about 2 hours. After it is confirmed that absorption of isocyanate groups in the infrared absorption spectrum had disappeared, the reaction was terminated to obtain an objective blocked isocyanate curing agent.

Production example 4

Preparation of pigment dispersed paste

26.9 parts of an epoxy quaternary ammonium salt type pigment dispersing resin (solid content 49%), 2.6 parts of carbon black, 30.2 parts of kaolin and 40.3 parts of ion exchanged water were put in a sand grind mill, and dispersed until the particle size becomes not more than 15 µm to obtain a lead-free pigment dispersed paste (solid content 46%).

Example 1

Preparation of cationic electrodeposition coating composition

210 parts of the amine modified epoxy resin of Production example 1, 57 parts of the blocked isocyanate curing agent of Production example 2 and 35 parts of the blocked isocyanate curing agent of Production example 3 were mixed so as to be uniform. After neutralizing this mixture with 5 parts of

acetic acid and 1 part of zinc acetate, the mixture was diluted by adding 100 parts of deionized water to obtain a main emulsion (solid content 36.0%).

278 parts of this main emulsion (solid content 100 parts), 85 parts of the pigment dispersed paste (solid content 39 parts) of Production example 4 and 332 parts of deionized water were mixed to obtain a cationic electrodeposition coating composition.

By means of a usual electrodeposition coating apparatus, a hard disk case made from an aluminum die-cast (aluminum die-cast having subjected to chromate treatment (Cr plating amount: 50 mg/m² in terms of chrome) was coated with the obtained cationic electrodeposition coating composition. Coating conditions were as shown in Table 1. The thickness of the cured coating was 20 μ m.

Table 1

Voltage (V)	180
Bath temperature (°C)	28
Curing temperature (°C)	205
Curing time (min.)	20

Static Tg (°C) of the cured coated film and weight loss by baking were evaluated, and the static Tg was 110°C and the weight loss by baking was 9.6%. It is to be noted that weight loss by baking corresponds to an amount of outgas of cured coated film, and the small value of weight loss by baking means the small amount of outgas.

Static Tg (°C) was measured according to the probe intrusion method using TMA-100 available from Seiko Instruments Inc. Measuring

conditions were as shown in Table 2. Preferably, the value of static Tg is not less than 100°C.

Table 2

Ploop diameter (mm)	1
Load (g)	50
Rate of temperature raise (°C/min.)	5

Weight loss by baking was calculated according to the calculation expression of Formula 1 after executing the following steps:

- (1) Precisely weigh the test panel (A).
- (2) Perform electrodeposition coating on the test panel.
- (3) After washing with water, dry the obtained wet coating at 105°C for 3 hours.
- (4) After cooling to the room temperature in a desiccator, precisely weigh (B).
- (5) Perform baking on the electrodeposition-coated test panel.
- (6) After cooling to the room temperature in the desiccator, precisely weigh (C).

$$D (\%) = [1 - (C - A) / (B - A)] \times 100$$

wherein D represents weight loss by baking, A represents weight of test panel before electrodeposition, B represents weight of test panel after drying and C represents weight of test panel after baking.

Preferably, the value of the weight loss by baking is not more than 15%.

Next, a salt water spray test (evaluation of corrosion resistance)

was conducted for the coated film obtained in the above, and filiform rust width from the cut portion was 3.4 mm.

The salt water spray test was conducted in the following manner. A cross cut reaching to the base was made on the coated panel having a cured coating using a knife, and 5% salt water was sprayed on the surface of the coated film at 35°C for 100 hours. Thereafter, the coated film was evaluated based on maximum width of one side (mm) of peeled portion of the coated film from the cut portion.

Example 2

Preparation of cationic electrodeposition coating composition

A cationic electrodeposition coating composition was prepared in the same manner as in Example 1 and evaluated except that a mixture of 42 parts of the blocked isocyanate curing agent of Production example 2 and 52 parts of the blocked isocyanate curing agent of Production example 3 was used as the blocked isocyanate curing agent. The evaluated results are shown in Table 3 and Table 4.

Comparative example 1

Preparation of cationic electrodeposition coating composition

A cationic electrodeposition coating composition was prepared in the same manner as in Example 1 and evaluated except that 85 parts of block isocyanate curing agent of Production example 2 was used alone in place of the combination of the blocked isocyanate curing agent of Production example 2 and the blocked isocyanate curing agent produce in Production example 3. The evaluated results are shown in Table 3 and Table 4.

Comparative example 2

Preparation of cationic electrodeposition coating composition

A cationic electrodeposition coating composition was prepared in the same manner as in Example 1 and evaluated except that 105 parts of blocked isocyanate curing agent of Production example 3 was used alone in place of the combination of the blocked isocyanate curing agent of Production example 2 and the blocked isocyanate curing agent produce in Production example 3. The evaluated results are shown in Table 3 and Table 4.

Table 3

Example No.	Static Tg (°C)	Weight loss by baking (%)
1	110	9.6
2	113	7.6
Comparative example 1	94	10.5
Comparative example 2	87	7.0

Table 4

Example No.	filiform rust width from cut portion (mm)
1	3.4
2	3.2
Comparative example 1	3.6
Comparative example 2	3.3

It was confirmed from the results of the above Examples that when a mixture of blocked alicyclic isocyanate and blocked isocyanate having aromatic ring is used as a curing agent of a cationic electrodeposition coating composition, it is possible to obtain a cured coating having a static Tg of not less than 100°C and causing a reduced amount of outgas, while keeping corrosion resistance comparable to that obtained by the conventional cationic

electrodeposition coating composition.

CLAIMS

1. A cationic electrodeposition coating composition for electronic parts which contains an amine modified epoxy resin and a blocked isocyanate curing agent as a binder component, wherein
the amine modified epoxy resin is an amine modified polyphenolpolyglycidyl ether type epoxy resin,
the blocked isocyanate curing agent is a mixture of the blocked isocyanate that is obtained by blocking alicyclic isocyanates and the blocked isocyanate that is obtained by blocking isocyanates having aromatic ring,
the coating composition substantially does not contain lead and tin.
2. The cationic electrodeposition coating composition for electronic parts according to claim 1, wherein said blocked isocyanate curing agent is a mixture of the blocked isocyanate that is obtained by blocking alicyclic isocyanates with oxime and the blocked isocyanate that is obtained by blocking isocyanates having aromatic ring with lower alcohol.
3. The cationic electrodeposition coating composition for electronic parts according to claim 1 or 2, wherein said blocked isocyanate that is obtained by blocking alicyclic isocyanates is that obtained by blocking isophorone diisocyanate with methyl ethyl ketoxime.
4. The cationic electrodeposition coating composition for electronic parts according to any one of claims 1 to 3, wherein ratio of said blocked isocyanate that is obtained by blocking alicyclic isocyanates and said blocked isocyanate that is obtained by blocking isocyanates having aromatic ring is 50/50 to 95/5 by solid weight.
5. The cationic electrodeposition coating composition for electronic

parts according to any one of claims 1 to 4, wherein ratio of said block isocyanate curing agent and said amine modified epoxy resin is 20/80 to 40/60 by solid weight.

6. The cationic electrodeposition coating composition for electronic parts according to any one of claims 1 to 5, wherein concentration of zinc ion in the coating composition is not less than 50 ppm.

7. The cationic electrodeposition coating composition for electronic parts according to claim 1, wherein an object to be coated is a computer hard disk case made of aluminum die-casting or magnesium die-casting.