

[54] **CATHODIC TREATMENT OF
CHROMIUM-PLATED SURFACES**

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[57] **ABSTRACT**

A method for treating a chromium-plated surface is provided characterized by the fact that a chromium-plated article is dipped as the cathode in a water-soluble or water-dispersible resin solution or dispersion prepared by diluting with water a resin salt of at least one synthetic polyamino resin with a water-soluble organic acid and/or a water-soluble inorganic acid, and then passing a direct current in the range of 10 – 300 volts through the aqueous bath so that there is formed a resin film on the chromium plated surface the chromium-plated surface is pretreated prior to the resin coating step by anodization in aqueous chromate solution or by heat treatment so that the surface electrode potential is greater than -0.42 volts.

13 Claims, No Drawings

CATHODIC TREATMENT OF CHROMIUM-PLATED SURFACES

This invention relates to the surface treatment of a chromium-plated surface. More particularly, this invention relates to a method of treating a chromium-plated surface characterized by the cathodic-deposition of a resin coating on the chromium-plated surface (used as the cathode) from an aqueous solution or dispersion of a resin salt comprising a thermosetting synthetic polyamino resin and an acid.

The term "chromium-plating" or the like used herein means all kinds of chromium plating known in the art of metal plating. The thickness of such chromium-plated layer is at least 0.01 micron, preferably at least 0.2 micron.

In conventional metal-plating, several metallic layers of copper, nickel or chromium are plated or electro-coated on a well ground and conditioned metallic article. The total thickness of such plated layer is usually about 5 to 50 microns. Particularly, the chromium plating is superior to any other metal plating in appearance, metallic-luster and corrosion resistance so that it is preferable that chromium is electroplated as a final finishing even on a copper or nickel plated surface to obtain corrosion-resistant plated articles. However, there is the disadvantage that numerous pinhole-like pores are present on such metal-plated surfaces so that it is difficult to prevent corrosion therethrough. In order to prevent such corrosion, it is necessary to make the thickness of all the plating layers at least about 50 microns. This would cause economic disadvantages including the increase in operative steps.

In order to overcome such disadvantage a coating of an organic material may be considered. However, with coating processes usually practiced in the coating industry such as brush coating, dipping or spraying, it is difficult to form a uniform film which can seal pores on the chromium-plated surface of an article with complicated form and which can retain a high grade appearance and an excellent metallic luster. Further, the adhesion of the organic coating on the metal surface is low with such conventional coating methods.

On the other hand, the formation of an organic coating by electrodeposition has a great advantage in the sealing of pores on the chromium-plated surface and in the formation of a uniform film layer. However, the resin to be used for the conventional electrodeposition coating composition generally has carboxyl groups and is used in the form of a water-dispersible resin in which the carboxyl groups are converted into salts with an alkaline substance. Thus the resin would be present in the form of anions in the aqueous medium. With the use of such an anionic type resin solution in the electrodeposition process, the chromium plated surface to be coated is treated as an anode. Therefore when direct current is passed the plated metallic chromium will be electrolytically dissolved out. In this case, if the plated article is a zinc die-casting or the like, the pores on the plated surface will become larger and more numerous so that the metallic ions of the base material and of the plated layers will dissolve out through such pores and will mix into the organic film. Therefore the organic coating film will be undesirably discolored and shrunk and its adhesion to the metal surface will be impaired. Further, due to the corrosion of the chromium-plating layer, the luster of the chromium-plated surface will be

deteriorated and, in some cases, the product value will be reduced by the partial exposure of the base or substrate metal.

The object of the present invention is to overcome all these drawbacks. Thus this invention relates to the improved surface treatment of a chromium-plated metal face. More particularly the present invention relates to a method for the surface treatment of a chromium-plated surface characterized by the fact that a chromium-plated article is dipped as a cathode in a water-soluble or water-dispersible resin solution or dispersion obtained by diluting with water a resin salt consisting of any one or mixture of two or more thermosetting synthetic polyamino resins and a water-soluble organic acid and/or a water-soluble inorganic acid or an aqueous solution thereof, and then passing a direct current through the aqueous bath so that there is formed an excellent resin film on the chromium-plated surface. According to the present invention the thick film character of the metal plating is enhanced in appearance without impairing the high grade appearance and excellent metallic luster of the chromium-plating. The total thickness of the metal-plating layers may be reduced. Further the resulting film has corrosion-resistance twice as high as that of a conventional plating layer of the same thickness, and the adhesion of the organic film to the chromium-plated surface is far higher than by any other coating method.

The synthetic polyamino resins to be used in the method of this invention are resins containing amino groups (such as primary, secondary or tertiary amino groups or quaternary ammonium groups) in the molecule, and are vinyl or acrylic copolymers containing amino groups as pendant groups, resinous polymers made by introducing amino groups by reacting dialkylamines or dialkanolamines with epoxy resins containing two or more epoxy groups in the molecule, polyester resins obtained by using alkanolamines as one component of polyols and cocondensing polybasic acids with the other polyols, polyurethane resins obtained by using alkanolamines as one component and cocondensing polyisocyanates with the other polyols or polyamide resins having terminal amino groups obtained by condensing stoichiometrically excess polyamines with polybasic acids.

In an aqueous solution or dispersion obtained by diluting with water a resin salt of such resin containing amino groups with a water-soluble organic acid and/or a water-soluble inorganic acid or an aqueous solution thereof, the resin acts as polymer cations and is therefore considered to be a cationic type resin. When a direct current is passed through the aqueous resin solution or dispersion, the resin is deposited on the chromium-plated surface used as the cathode. Therefore, if an insoluble anode such as, for example, lead, carbon or stainless steel is used the electrolytic dissolution of metal will be prevented.

If desired, the amino groups contained in such resin can be alkylated by a known method and can be finally converted to quaternary ammonium groups. However, in the present invention, it is not always necessary to convert the amino groups into quaternary ammonium salts. It is desirable that the resin to be used be thermosetting or curable. In such a case, self-cross-linkable functional groups can be introduced in the resin itself. It is also possible to blend a cross-linking agent with the resin, such as for example, a lower alcohol (e.g. methanol, butanol, etc.) ether of a condensate of formalde-

hyde with phenol, melamine or urea, or an epoxy compound or a blocked isocyanate. The amount of such cross-linking agent may be 5 – 30 % by weight based on the total resin composition.

The acid component to be used for forming a resin salt with the above mentioned synthetic polyamino resin is selected from water-soluble organic acids such as formic acid, acetic acid, propionic acid, lactic acid, malonic acid or citric acid or water soluble inorganic acids such as hydrochloric acid, phosphoric acid or sulfuric acid. If desired, a mixture of two or more of them may be used. The amount of the acid to be used is preferably 0.3 to 1.0 equivalent for 1.0 equivalent of the amino group of the synthetic polyamino resin. Below 0.3 equivalent, the water-dispersibility of the resin salt will be so low that the stability of the diluted resin solution will be low. Above 1.0 equivalent, the redissolution of the resin composition deposited on the chromium-plated surface will be considerable and the deposition of bubbles developed in the electrolysis on the resin coating will be considerable.

The concentration of the resin in the aqueous resin solution or dispersion prepared by diluting the above mentioned resin salt with water is preferably 1 to 20 % by weight. Below 1 % by weight, the deposition of the resin on the cathode will not be easy. Above 20 % by weight, the resin solution will become sticky.

The temperature of the bath (i.e. the aqueous resin solution or dispersion) is preferably 10 to 50°C.

In carrying out the cathodic electrodeposition the aqueous resin solution or dispersion is held in an electrodeposition cell or tank made of a material not corroded by the resin solution or dispersion. A carbon rod or lead plate is used as an anode and a chromium-plated article to be treated is used as a cathode. These electrodes are dipped into the electrodeposition bath and a potential difference of 10 to 300 volts is applied between the electrodes while stirring the bath. The treating time may be properly varied depending on the particular object but is generally 10 seconds to 5 minutes.

Then the coated cathode is taken out of the tank, washed with water and is baked and dried to obtain a resin coated chromium-plated surface high in both appearance and performance.

It has further been found that the surface treatment effect is further improved if the chromium-plated surface is pretreated prior to the above mentioned electrodeposition of the resin. Thus, by this pretreatment the adhesion of the electrodeposited organic resin layer on the chromium-plated surface is improved and further the appearance of the resin layer is improved.

This pretreatment is conducted by subjecting the chromium-plated surface to (1) anodic treatment in an aqueous solution of chromic acid, (2) heat treatment at a high temperature or (3) exposure to air for a long period of time, so that the electrode potential (which is a value measured at 15 seconds after the beginning of the measurement by using a saturated calomel electrode as a standard in a buffer solution of 0.1 mol of citric acid, 0.2 mol of sodium hydrogen phosphate and a pH of 4.7 at a temperature of 25°C., and is referred to merely as a potential hereinafter) of the chromium-plated surface becomes more noble than -0.42 volt.

As a result of various researches on the treatment of a chromium-plated surface by anodic electrodeposition processes, we have found that the adhesion of the cationic type resin film to the chromium-plated surface is

influenced by or depends on the state of the chromium-plated surface. In other words, the adhesion has a selectivity for the surface state of the chromium-plating. Such selectivity is determined by the surface potential of the chrom-plate. On the other hand, it has been confirmed as a result of CASS tests (Copper-Accelerated Acetic Acid Test, JIS D-0201) and sight tests that the adhesion of an organic film to a metal face is related to the uniformity of the appearance and the degree of the corrosion resistance of the film.

The state of the chromium-plated surface shall be explained more concretely with numerical values. It has been found that, when a chromium-plating has a surface state of a potential higher (more noble) than -0.42 volt, the adhesion of the film thereto is very favorable.

We have further found that the potential of a chromium-plated surface may be made more noble than -0.42 volt if the chromium-plated surface is subjected to (1) anodic-electrolytic treatment in 0.1 – 5 % solution of chromic acid, or (2) heating and drying at a high temperature or (3) air at the normal temperature for a long time, to modify the surface of the chromiumplated layer. When the abovementioned electrodeposition of organic resin is conducted after this pretreatment there is obtained a resinous coating film having such strong adhesion and high corrosion-resistance as have never been obtained before.

The pretreatment or surface modification of the chromium-plated face prior to the electrodeposition of the organic resinous film thereon will be explained in more detail as follows.

The first method is the anodic-electrolytic treatment of the chromium surface of a chromium-plated article in an aqueous solution of chromic acid or dichromate. Usually the electrolysis is carried out at an anode current density of 0.1 to 5 amperes/dm.² at the normal temperature for 20 to 180 seconds in 0.1 – 5 % solution of chromic acid or dichromic acid so that the potential of the chromium-plated surface becomes nobler than -0.42 volt.

However, the above mentioned particular conditions for the anodic-electrolysis are not always critical. Thus in case the treatment is carried out under conditions other than those mentioned above, the potential of the chromium-plated surface can be rendered more noble than -0.42 volt.

However, if the electrolysis is conducted for a longer time and/or the anode current density is made higher, the chromium-plating itself will tend to dissolve to expose the base or substrate metal, so that the chromium-plating will have to be made thicker to prevent it and therefore such conditions will be not practical. On the other hand, if the anode current density is made lower, it will be necessary to conduct the electrolysis for an extremely long time.

In actual operation it is preferable to conduct this anodic electrolysis just after the chromium-plating step. After the anodic electrolysis the pretreated article is subjected to washing with water, cathodic electrodeposition, washing with water and drying in the mentioned order.

The second method of the pretreatment is to heat the chromium-plated surface at a high temperature prior to the electrodeposition of the resinous coating film. Thus, after the chromium-plating, the plated article is washed with water and then heated and dried at a high temperature. The temperature at which such heating is

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conducted varies depending upon the time and the state of the chromium-plating itself to be treated and therefore the temperature and time can not be definitely specified. However, it is found that, as a general standard, they may be expressed by the product $(^{\circ}\text{C.}) \times (\text{min.})$. The minimum standard value is 3000 $(^{\circ}\text{C.}) \times (\text{min.})$. For example, when the heating is conducted at 50°C. the minimum time required is 60 minutes or longer, and when heated and dried at 100°C. the time required would be at least 30 minutes. In case of 200°C. the time required is at least 15 minutes. The upper limit of the temperature is 300°C. This heat treatment can be conducted in air or in hot water.

Another pretreatment is to expose the chromium-plated surface to air at the room (or "normal") temperature (e.g. $10^{\circ} - 35^{\circ}\text{C.}$) for a long time. The effect of this treatment is considered to be that the chromium-plated surface will be oxidized by oxygen in air so that the potential becomes nobler than in the case that such exposure is not carried out. Therefore, by this treatment the potential can be made more noble than -0.42 volt depending on the degree of the oxidization, that is, the time of exposure. In this case, the time required to make the potential nobler than -0.42 volt is at least 24 hours. If the exposure time is shorter, for example, 18 hours, usually the surface potential of the chromium-plating will be only -0.46 volt. After this pretreatment, the chromium-plated article may be subjected to the electro-deposition mentioned before.

If the chromium-plated surface modified or pretreated as mentioned above so that the surface potential may be more noble than -0.42 volt is then coated with the above described thermosetting synthetic poly-amino resin film by the cathodic electrodeposition, the adhesion of the resin film to the chromium surface is improved and therefore a product having a higher corrosion resistance is obtained.

The effect of this pretreatment will be demonstrated as follows. Thus, in order to facilitate the comparison, there were used test pieces prepared by chromium plating to a thickness of 0.5 micron in a sargent bath (normal chromium-plating bath) iron pieces (2 dm.^2) which have been copper-plated to a thickness of 10 microns and bright-nickel-plated by a thickness of 5 microns. As for the cation type resin, there was used a resin prepared by introducing amino groups by making a secondary amine react with an acrylic copolymer. An aqueous solution of the acetate of the resin at a pH of 5.0 and a resin concentration of 10 % by weight was used a cathodic-electrodeposition bath.

The electrodeposition was conducted at a voltage of 70 volts for 1 minute at a temperature of 20°C. After the electrodeposition the coated film was baked at 200°C. for 30 minutes.

In the above the chromium-plated surface was not pretreated or modified, and chromium-plating, water-washing (or water-washing and hot-water-washing), cathodic-electrodeposition, water-washing and baking were conducted in the mentioned order. The potential of the chromium-plated surface was -0.49 to -0.54 volt. The corrosion-resistance of the resulting resin film had a rating number of 7 in 5 cycles of the CASS Test.

In the case of carrying out the pretreatment i.e., anodic-electrolysis, chromium-plating, anodic-electrolysis, water-washing, cathodic-electrodeposition and baking were conducted in the mentioned order. The anodic-electrolysis was effected at 25°C. , with anode current density of 2 amperes/ dm.^2 and for 30 seconds

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in 1 % aqueous solution of chromic acid. The potential of the chromium-plated surface became -0.35 volt by this pretreatment. The adhesion of the resin film was strong and the corrosion-resistance had a rating number of 10 in 5 and 7 cycles of the CASS Test.

As another pretreatment the chromium-plated surface was exposed to the atmosphere (ambient air) for a long time. In this case, chromium plating, water-washing, exposure to air, cathodic-electrodeposition, water-washing and baking were conducted in the mentioned order. When exposed to air for 24 and 48 hours, the potentials of the chromium plated surface became respectively -0.39 and -0.34 volt. The appearance of the obtained resin film was uniform and the corrosion-resistance had rating numbers of 10 in 5 cycles and 9 in 7 cycles of the CASS Test.

Still another pretreatment i.e. heat-treatment at a high temperature was conducted. In this case, chromium-plating, water-washing, high temperature heat-treatment, cathodic-electrodeposition, water-washing and baking were conducted in the mentioned order. Thus the chromium-plated surface was heated at 50°C. for 60 minutes, at 100°C. for 30 minutes and at 200°C. for 15 minutes respectively. By this pretreatment the potential of the chromium-plated surface became respectively -0.37 , -0.32 and -0.27 volt. The resulting cathodic-electrodeposited film was uniform and smooth in appearance, high in the adhesion and had corrosion-resistance of a rating number of 10 in 5 cycles of the CASS Test.

As apparent from the above mentioned comparative tests, when the chromium-plated surface is pretreated or modified, the potential of the chromium-plated surface can be made nobler than -0.42 volt and, when the so pretreated surface is subsequently subjected to the cathodic-electro-deposition treatment, a film excellent in appearance and performance is obtained.

As still another aspect of this invention we have also found a means of further improving the excellent appearance and metallic luster of a chromium-plating. Thus, according to this invention, it is preferable to conduct a special after-treatment after an organic resin film has been formed by the cathodic-electrodeposition.

More particularly, after an organic resin film is formed on the chromium-plated surface by the before mentioned cathodic-electrodeposition but before the baking or curing of the film, there is conducted an after-treatment which comprises contacting the resin film with an aqueous solution or dispersion containing one or more of anti-oxidants, surface-active agents, organic solvents, acids and bases.

In the electrodeposition coating step, in response to the differences in surface states of the base or substrate of the article, for example, insufficient defatting, presence of stains, flaws, differences in rolling and the presence of different kinds of metals due to welding, etc. the electric characteristics of the surfaces are different and hence the state of the electrodeposited film will be much influenced thereby. For example, if the base metal to be plated is perfectly cleaned and ground and then chromiumplated the resulting surface state may be not so bad. However, for example, when a zinc die-casting is plated, the resulting surface state of the chromium-plating will be poor from an electrochemical viewpoint. Therefore, in the case of coating by electro-deposition on a chromium-plated surface, it will be necessary to take care to prevent the product value

from being reduced by these influences. Further, since the smoothness and luster in the appearance of a chromium-plated surface are known to be excellent it is necessary not to impair these favorable effects by applying an organic film coating thereon.

Further, in the production of the thermosetting synthetic polyamino resins to be used in the present invention, a basic nitrogen-containing resin is reacted with an acid to form a salt, which is dissolved or dispersed in water. When the nitrogen-containing component is oxidized, it will tend to become yellowish. When a light colored or colorless transparent coating film electrodeposited from such aqueous solution or dispersion of the resin is heat-treated or baked to be cured in the final step, the surface of the film is likely to be oxidized so that the film tends to become yellowish. Further, the so called orange peel phenomenon likely to occur.

We have found that these drawbacks are overcome if the electrodeposited resin film is treated (before being baked or cured) with an after-treating agent. By applying this treatment, not only are the excellent appearance and metallic luster of the chromium-plating not impaired but also no coated appearance results, so that the thick film character of the plated layer increases.

The after-treatment agents that can be used are surface active agents, antioxidants and organic solvents. They may be used respectively alone or as mixed. A proper amount of the same is used as diluted with water.

In carrying out the after-treatment, the electrodeposition resin coated article is washed with water and then dipped for several seconds to about 10 minutes in the above described aqueous after-treating agent. Then the coated film is subjected to setting or is preheat-treated at about 40° – 90°C. and then subjected to final baking or curing.

The surface active agent used in this after-treatment is effective in removing the electrolysis gas deposited on the electrodeposited film and in improving the smoothness of the coated film surface. By both of these effects, the nonuniformity of the film is eliminated and the colored specks produced by the combination of the orange peel phenomenon and yellowing phenomenon are effectively prevented. Further there is also an additional effect of improving wear-resistance such as the surface slip and scratching resistance of the finished coating film.

The useful surface active agents are silicone surface active agents, anionic surface active agents, cationic surface active agents, nonionic surface active agents and amphoteric surface active agents. The total concentration of such surface active agent is about 0.001 to 2.0 % by weight.

The antioxidants that may be used as the aftertreating agent are those having an effect of preventing the cationic type resin from being discolored by the oxidation. Such antioxidant is easily and uniformly adsorbed on the surface of the electrodeposited coating film surface so that the oxidization of the coating film surface by the heat-treatment at the time of baking or curing is prevented. Therefore, in a cationic resin coating film of a thickness not more than about 25 microns, the yellowing phenomenon at the time of baking or curing of the coated film can be substantially prevented. Therefore, it is not necessary to add an antioxidant into the resin composition for the electrodeposition so that the bath control or handling is easy.

Examples of useful antioxidants are those of phenol derivatives or phosphites. The concentration thereof in the after-treatment bath is about 0.01 to 2.0 % by weight.

5 The organic solvent that can be used as an aftertreating agent promotes the leveling effect of the coated film by slightly dissolving the electrodeposited film surface, removing the electrolysis bubbles on the surface and giving a fluidity so that the nonuniformity of the film surface is eliminated and the same effect as of the surface active agent may be obtained even against color specks. The organic solvent also has a role of helping the surface active agent and antioxidant to uniformly disperse in the aftertreating bath.

15 Therefore, in selecting such an organic solvent, it is necessary to consider the affinity of the organic solvent with the electrodeposited coating film. Further, since the after-treating agent is generally used as diluted with water, it is preferable that the solvent be compatible with water. Further, the boiling thereof at the time of the subsequent baking or curing should be kept minimum. Therefore it is preferable that the organic solvents are those having a high boiling point, lyophilicity and hydrophilicity (that is, having a surface active effect). For this purpose, ethylene glycol monobutyl ether or the like is most effective.

25 However, in the case of using a mixture of organic solvents, any solvent having any role of the above mentioned organic solvents including hydrophobic organic solvents can be used. For example, glycol ethers, alcohols, ketones and esters may be used.

30 The total concentration of such organic solvent in the after-treating bath is 1 to 90 %, preferably 5 to 70 % by weight.

35 When it is desired that the cationic resin coating film be baked or cured at a lower temperature or its surface hardness be increased, it is effective to add a curing catalyst or cross-linking agent for the resin in the after-treatment bath.

40 Thus when a lower alcohol ether of a condensate of formaldehyde with phenol, melamine or urea is blended with the cationic polyamino resin salt for the electro-deposition coating, an acid useful for promoting the curing of the condensate may be used as the after-treating agent. Examples of such acid catalyst are phthalic anhydride, trimellitic anhydride, pyromellitic anhydride, oxalic acid, etc. which are well known in the art as catalysts for promoting the curing of formaldehyde resins. The concentration of the acid may be about 0.1 – 5.0 % by weight in the after-treating liquid. By effecting this acid after-treatment the temperature required for baking or curing the deposited resin film may be lowered by about 20°C. or more.

55 Further, when the cationic resin used for the electrodeposition contains epoxy groups as functional groups, it is preferable to add to the after-treating liquid a cross-linking or curing agent well known for curing epoxy resins, e.g. bases such as amines and amides. More particularly examples thereof are dicyandiamide, dibutylamine, etc. The concentration of such base in the after-treating liquid is about 0.1 – 5.0 % by weight. When the after-treatment with such base is effected, the subsequently baked or cured resin film is increased in the hardness from 2H (not after-treated) to 3H, or sometimes even to 4H.

65 The invention will be further explained by means of the following Examples wherein all parts and percentages are by weight unless otherwise specified.

EXAMPLE 1

17.5 parts of styrene, 35 parts of glycidyl methacrylate and 35 parts of 2-ethylhexyl acrylate were polymerized by a solution-polymerizing process in isopropyl alcohol by using a polymerization initiator. The obtained copolymer was modified with 12.5 parts of dinormal propylamine and the formed thermosetting polymer was diluted with water to which malonic acid had been added to adjust the resin solution concentration to 10 % by weight. At this time, the pH was 4.0 and a substantially transparent solution was obtained. Then 3.5 liters of this resin solution were put into an electro-deposition tank (10 × 20 × 20 cm.). A carbon rod of a diameter of 10 mm. was fixed as an anode to one end of the tank. The bath solution temperature was made 25°C., a chromium-plated sheet (made by plating an iron sheet with copper 8 microns thick, bright nickel 8 microns thick and chromium 0.3 micron thick, the total thickness of the plated layer being smaller than in the usual plating) of 1 dm.² was dipped in the bath as the cathode. Then a direct current was passed through the bath by the use of a constant voltage system. After the current was passed at 50 volts for 1 minute, the coated article (cathode) was taken out of the bath, water-washed and baked in a hot air drying oven at 170°C. for 30 minutes to obtain a sheet with a uniform resin coating having a pencil hardness of 2H, a film thickness of 5 microns and excellent appearance. Upon CASS Test (JIS D-0201), the corrosion-resistance was rating number 10 in 4 cycles and rating number 9 in 5 cycles. In contrast, when the resin-coating is not effected the corrosion-resistance is less than rating number 9 in 2 cycles.

EXAMPLE 2

20 parts of dimethylaminoethyl methacrylate, 15 parts of 2-hydroxyethyl methacrylate, 25 parts of methyl methacrylate and 40 parts of 2-ethylhexyl acrylate were polymerized in isopropyl alcohol by using an azo compound as a polymerization initiator to obtain a solution of a copolymer (solids content 65 %).

30 % by weight of a 65 % solution of a blocked isocyanate and 70 % by weight of the above prepared copolymer solution were well mixed together and the mixture was diluted with water to which formic acid had been added to adjust the resin solution concentration to be 15 % by weight. At this time, the pH was 4.3 and the solution was white-turbid. This resin solution was used as a bath (25°C.) in the same apparatus as in Example 1. A chromium-plated sheet (made by plating an iron sheet with a copper thickness of 8 microns, semi-bright nickel of a thickness of 5.5 microns, bright nickel of a thickness of 2.5 microns and chromium of a thickness of 0.3 micron) of 1 dm.² was dipped in the bath as the cathode. An electric current was passed therethrough by means of a direct current constant voltage system. After the current was passed at 70 volts for 1 minute, the resin-coated article was taken out of the bath, water-washed and then baked in a hot air drying oven at 160°C. for 30 minutes to obtain a sheet with a uniform resin coating having a pencil hardness of H, a film thickness of 7 microns and excellent appearance. The corrosion-resistance of the resulting sheet was of a rating number of 9 in 4 cycles but the one not treated by the present method was of a rating number of 9 in 2 cycles.

EXAMPLE 3

An iron-made bicycle lamp case of 3 dm.² was plated with a thickness of 10 microns copper, bright nickel thickness of 6 microns and chromium thickness of 0.4 micron. Immediately thereafter this article was subjected to anodic-electrolysis with 1 % solution of chromic acid at 25°C. and an anode current density of 0.5 ampere/dm.² for 40 seconds and was immediately water-washed for 2 minutes to prepare an article having a modified chromium-plated surface.

37 parts of glycidyl methacrylate, 17.5 parts of methyl methacrylate and 37 parts of butyl acrylate were polymerized in an ordinary manner in isopropyl alcohol by using an azo compound as a polymerization initiator. Then 7.5 parts of diethanolamine were reacted with the above prepared copolymer. 40 parts of ethylene glycol monobutyl ether and 34 parts of 10 % acetic acid were added to and well mixed with the resulting resin solution. Deionized water was added to the resin solution to adjust the resin concentration to 10 %. At this time, the pH of the solution was 5.0.

The above modified chromium plated article was subjected to the electrodeposition in 3.5 liters of the above prepared bath at 20°C. at a voltage of 75 volts for 1 minute in the same apparatus as in Example 1. Then the article was water-washed for 1 minute and was dried and baked at 200°C. for 30 minutes.

The hardness of the resulting film was 2 H, the appearance was uniform, the adhesion was very high and the corrosion-resistance was of rating numbers of 10, 10 and 9 respectively in 5, 7 and 9 cycles upon the CASS Test.

EXAMPLE 4

The same article and resin solution as in Example 2 were used and the modification (or pretreatment) was conducted in the same manner as in Example 3. Then the electrodeposition was conducted under the same conditions as in Example 3 except that the temperature was 20°C., voltage was 70 volts and the time was 1 minute. The same excellent results as in Example 1 were obtained.

EXAMPLE 5

The same chromium-plated sample as in Example 3 was washed with water for 1 minute and with hot water at 50°C. for 1 minute after the chromium-plating. Then the sample was left in air for 24 hours at 25°C., was then subjected to the electrodeposition in the same manner as in Example 3. Then the article was immediately water-washed for 1 minute and was dried and baked at 200°C. for 40 minutes.

The hardness of the resulting film was higher than 2 H and both adhesion and appearance were excellent. The corrosion resistance was of rating numbers 10 in 5 cycles and 9.5 in 7 cycles according to the CASS Test.

EXAMPLE 6

The same chromium-plated sample as in Example 3 was used. Immediately after the chromium-plating the sample was washed with water for 1 minute and with hot water for 1 minute, and then heated at 100°C. for 30 minutes. Then the pretreated sample was subjected to the cathodic-electro-deposition in the same bath and under the same conditions as in Example 3. After the electrodeposition, the sample was water-washed for 1

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minute and was dried and baked at 200°C. for 30 minutes.

The hardness of the resulting film was 2 H and the adhesion and appearance of the film was excellent. The corrosion-resistance was of a rating number of 10 in 5 cycles according to the CASS Test.

EXAMPLE 7

As an after-treating agent, 2,6-di-t-butyl-4-methyl phenol (a phenolic antioxidant) was dissolved in ethylene glycol monobutyl ether, and a water-soluble silicic surface active agent was added thereto and uniformly dissolved in the solution. Then the solution was diluted with water so that the respective concentrations become 0.3 % of the antioxidant, 0.2 % of the surface active agent and 30 % of the organic solvent.

34.5 parts of glycidyl methacrylate, 17.2 parts of styrene and 34.5 parts of 2-ethylhexyl acrylate were polymerized in an ordinary manner in 35 parts of isopropyl alcohol by using azobisisobutyronitrile as a polymerization initiator. Then 13.8 parts of diisopropanolamine were added together with 18 parts of ethylene glycol monobutyl ether to react with the obtained copolymer.

30 parts of ethylene glycol monobutyl ether and 45 parts of 10 % acetic acid were added to and well mixed with the above prepared resin solution and deionized water was added thereto to adjust the resin concentration to be 10 %. The pH at this time was 4.8. In the apparatus in Example 1, an article to be coated (made by nickel-chromium-plating a soft steel sheet and left for 24 hours in air at 20°C.) was used as the cathode and a carbon rod was used as the anode. A direct current of a voltage of 70 volts was passed through the cell at 20°C. for 1 minute. A resin film was electrodeposited on the chromium plated article. The article was water-washed, was then dipped in the above mentioned after-treating solution at 20°C. for 30 seconds. The after-treated article was then predried at 50° to 60°C. for 5 minutes and was heat-treated at 200°C. for 30 minutes to obtain a cured resin coating film (thickness 5 microns). The article perfectly retained the metallic luster of the chromium-plating, gave no painted sense and the surface pencil hardness was 3 H.

For comparison the same procedure was repeated except that the after-treatment was not conducted. The resulting resin film was lightly yellowish on the surface and was a little lower in surface smoothness.

EXAMPLE 8

As an after-treating agent, a peroxide decomposing agent and a phenolic antioxidant were dissolved in diethylene glycol monobutyl ether. An oil-soluble silicic surface active agent and a nonionic surface active agent were added thereto and uniformly dissolved in the solution. Then the solution was diluted with water so that the respective concentrations became 0.1 % of the peroxide decomposing agent, 0.2 % of the antioxidant, 0.01 % of the silicic surface active agent, 0.1 % of the nonionic surface active agent (oleylpolyethyleneglycolether) and 25 % of the organic solvent.

A direct current was passed at a voltage of 150 volts through the same chromium-plated sheet in the same bath as in Example 7 at a bath temperature of 25°C. for 2 minutes. The resin-coated sheet was water-washed, was dipped in the above mentioned after-treating solution at 25°C. for 2 minutes, was then preheated at 80°

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to 90°C. for 5 minutes and was then heat-treated or baked at 200°C. for 30 minutes to obtain a sheet with a uniform resin film (thickness about 25 microns) which is excellent in the smoothness, and is substantially colorless and has a pencil hardness of 2 H.

The same procedure was repeated except that the after-treatment was not conducted. The resulting resin film was yellowish and had an orange peel.

EXAMPLE 9

34.5 parts of glycidyl methacrylate, 17.2 parts of styrene and 34.5 parts of 2-ethylhexyl acrylate were polymerized together in an ordinary manner in 35 parts of isopropyl alcohol in the presence of an azo compound (polymerization initiator). Then 13.8 parts of diisopropanolamine were added together with 18 parts of ethylene glycol monobutyl ether to react with the above obtained copolymer.

A commercial water-soluble melamine resin (alcohol ether of melamine-formaldehyde condensate, solids content 70 %) was added to the above prepared copolymer solution in such an amount that the solids ratio (copolymer: melamine resin) is 75:25. Then 30 parts of ethyleneglycol monobutyl ether and 45 parts of 10 % acetic acid solution were added thereto and the mixture was diluted with deionized water to prepare a resin solution (pH 4.9) with a resin solids content of 10 %.

With the use of this resin solution the electro-deposition was conducted in the same manner as in Example 7. After washing with water the resin coated sample was dipped for 60 seconds at 20°C. in an after-treating solution which is a 25 % aqueous solution of ethyleneglycolmonobutylether and then dipped for 15 seconds at 20°C. in a second after-treating solution which was prepared by dissolving a phenolic antioxidant and a silicone surfactant into a mixed solvent (ethyleneglycolmonobutyl ether 20 parts, ethyleneglycolmonoethyl ether 40 parts, n-butanol 20 parts and isopropanol 20 parts), diluting the solution with water and then adding trimellitic anhydride thereto. The concentrations of various ingredients in the second after-treating solution were organic solvents 50 %, antioxidant 0.2 %, surfactant 0.02 %, and trimellitic anhydride 1.0 %.

After these after-treatments the coated sample was preheated at 70°–80°C. for about 5 minutes and then baked at 180°C. for 30 minutes to obtain a sheet with a resin coating film (thickness 7 microns) having a surface pencil hardness of 3 H. The chromium-plated surface luster was perfectly retained.

For comparison the same procedure was repeated except that the after-treatments were not conducted. The resulting resin film had a surface pencil hardness of H – 2 H.

EXAMPLE 10

The copolymer prepared in Example 9 was modified by diisopropanolamine in the same manner as in Example 9. The modified resin was neutralized by 45 parts of 10 % acetic acid solution and then diluted with deionized water to obtain a resin solution (resin solids content 10 %, pH 4.8).

With the use of this resin solution the electro-deposition and subsequent washing were conducted in the same manner as in Example 9. Then the coated sample was after-treated in the same manner as in Example 9 except that the second after-treating solution contained 0.5 % of dicyandiamide instead of 1.0 % of trimellitic anhydride. After this after-treatment, the coated sam-

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ple was preheated at 70°– 80°C. for about 5 minutes and then baked at 200°C. for 30 minutes to obtain a sample with a resin coating film (thickness 5 microns) having a surface pencil hardness of 4 H. The luster of the chromium-plated surface was not impaired by the coating.

For comparison the same procedure was repeated except that the after-treatment was not conducted. The resulting resin film was lightly yellowish and had a surface pencil hardness of 2H – 3H.

What is claimed is:

1. A method for treating a chromium-plated surface characterized by the fact that a chromium-plated article having an uppermost chromium-plated layer of a thickness of at least 0.2 micron and adjacent thereto, an intermediate nickel or nickel-alloy layer, is dipped as the cathode in a water-soluble or water-dispersible resin solution or dispersion prepared by diluting with water a resin salt of at least one synthetic polyamino resin and a water-soluble organic acid, a water-soluble inorganic acid or a mixture of said acids and then passing a direct current in the range of 10–300 volts through the aqueous bath so that there is formed a resin film on the chromium plated surface.

2. A method as claimed in claim 1 wherein after the electrodeposition the resin-coated article is subjected to an after-treatment with an aqueous treating agent, said treating agent being selected from the group consisting of antioxidants, surface-active agents, organic solvents, acids and bases, and is thereafter baked or cured.

3. A method as claimed in claim 2 wherein the aqueous treating agent for the after-treatment contains an anti-oxidant selected from the group consisting of phenolic-type antioxidants and phosphite-type antioxidants at a concentration of 0.01 to 2.0% by weight.

4. A method as claimed in claim 2 wherein the aqueous treating agent for the after-treatment contains a surface-active agent selected from the group consisting of silicone oils and anionic, cationic, nonionic and amphoteric surface-active agents at a concentration of 0.001 to 2.0 percent by weight.

5. A method as claimed in claim 2 wherein the aqueous treating agent for the after-treatment contains an organic solvent selected from the group consisting of glycol ethers, glycol ether esters, alcohols, ketones and esters at a concentration of 1 to 90 % by weight, preferably 5 to 70 % by weight.

6. A method as claimed in claim 2 wherein the aqueous treating agent for the after-treatment contains an acid selected from the group consisting of phthalic anhydride, trimellitic anhydride, pyromellitic anhydride and oxalic acid at a concentration of 0.1 – 5.0 %, preferably 0.3 – 4.0 % by weight.

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7. A method as claimed in claim 2 wherein the aqueous treating agent for the after-treatment contains a base selected from the group consisting of dicyandiamide and dibutylamine at a concentration of 0.1 – 5.0 %, preferably 0.3 – 4.0 % by weight.

8. A method as claimed in claim 1 wherein the chromium-plated surface is pretreated before the electrodeposition so that the surface electrode potential as defined herein before has a value higher than –0.42 volt by means of an electrochemical or physical treatment.

9. A method as claimed in claim 8 wherein the electrochemical treatment is conducted by the anodic-electrolysis of the chromium-plated surface in an aqueous solution selected from the group consisting of chromic acid, chromate or dichromate.

10. A method as claimed in claim 8 wherein the physical treatment is conducted by heating the chromium-plated surface such that the product of the temperature and time of treatment is at least 3000°C-min. and the upper limit of temperature is 300°C.

11. A method as claimed in claim 8 wherein the physical treatment is conducted by exposing the chromium-plated surface to air at the normal temperature for at least 24 hours.

12. A method as claimed in claim 1 wherein the synthetic polyamino resin is a resin containing primary, secondary, or tertiary amino groups or quaternary ammonium groups or mixtures of these groups in the molecule, and is selected from the group consisting of (A) a vinylic or acrylic copolymer containing amino groups as pendant groups, (B) a resinous polymer made by introducing amino groups by making a dialkylamine or dialkanolamine react on an epoxy resin containing two or more epoxy groups in the molecule, (C) a polyester resin obtained by using an alkanolamine as one component of a polyol and cocondensing a polybasic acid with the other polyol, (D) a polyurethane resin obtained by using an alkanolamine as one component and cocondensing a polyisocyanate with the other polyol and (E) a terminal amino group-containing polyamide resin obtained by condensing a stoichiometrically excess polyamine with a polybasic acid at a solid part concentration in the electrodepositing bath solution in a range of 1 to 20 percent by weight.

13. A method as claimed in claim 1 wherein said water-soluble organic acid and water-soluble inorganic acid are selected from the group consisting of formic acid, acetic acid, propionic acid, lactic acid, malonic acid, citric acid, hydrochloric acid, phosphoric acid, and sulfuric acid and wherein said water-soluble organic acid, water-soluble inorganic acid or mixture thereof is employed in an amount of 0.3 to 1.0 equivalent for 1.0 equivalent of the amino groups in the synthetic polyamino resin.

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