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METHOD FOR COATING THE SURFACE OF A METALLIC MATERIAL

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U.S. Cl. 204—181 14 Claims

ABSTRACT OF THE DISCLOSURE

A method for coating the surface of a metallic material which comprises immersing the metallic surface in an aqueous composition comprising a film-forming polymer, an acid and an oxidizing agent, passing a direct electric current between the metallic surface, as a primary electrode, and a secondary electrode and withdrawing the metallic surface from the aqueous composition, followed by baking the coated surface.

The present invention relates to a method for coating the surface of a metallic material. More particularly, it relates to a method for forming a uniform and smooth film of polymer firmly adhered on the surface of a metallic material, particularly of a ferriferous or zinciferous material, in a short time.

According to conventional electro-deposition coating processes where an electric current of about 100 to about 200 volts is usually applied, the formation of a uniform and smooth film on the surface of a metallic material with an aqueous dispersion of a film-forming polymer is difficult. Particularly when a lower bath voltage is applied, this tendency becomes remarkable.

It has now been found that a uniform and smooth film of sufficient and satisfactory thickness can be formed firmly on the surface of a metallic material, particularly of a ferriferous or zinciferous material, in a very short time by the use of a certain, specific aqueous composition comprising a film-forming polymer, an acid and an oxidizing agent and the application of a direct electric current of low voltage.

In accordance with the present invention, there is provided a method for coating the surface of a metallic material which comprises immersing the metallic surface in an aqueous composition comprising a film-forming polymer, an acid and an oxidizing agent, passing a direct electric current between the metallic surface, as a primary electrode, and a secondary electrode and withdrawing the metallic surface from the aqueous composition, followed by baking the coated surface.

The material to be coated on the surface by the method of this invention is a metallic one, particularly a ferriferous or zinciferous one. The term "ferriferous" herein used is intended to mean iron, steel and other iron alloys wherein iron is the principal constituent (such as especially cold- and hot-rolled steel alloys with minor amounts of carbon, silicon and manganese) but excludes the so-called "stainless steel." The term "zinciferous" is intended to mean not only zinc and zinc-alloys wherein zinc is the principal con-

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stituent but also galvanized metal, especially both hot-dipped and electrogalvanized iron steel.

The aqueous composition used for coating in the method of this invention comprises a film-forming polymer, an acid and an oxidizing agent as the essential components.

The film-forming polymer is normally used in the form of an aqueous dispersion stable over a period of at least 24 hours at a pH range of about 1.6 to about 5.0. Examples of the aqueous dispersion which is commercially available are styrene-butadiene copolymer emulsion ("Hycar LX 407" manufactured by Nihon Geon Co., Ltd.; "Pliolite 491" manufactured by Goodyear Rubber & Chemical Corp.), acrylic copolymer emulsion ("Hycar LX 814" manufactured by Nihon Geon Co., Ltd.; "Polysol AP 300" manufactured by Kobunshi Kagaku Kogyo Co., Ltd.), ethylene-vinyl acetate copolymer emulsion ("Polysol EVA P 1" manufactured by Kobunshi Kagaku Kogyo Co., Ltd.), polyethylene emulsion ("Poly-em 40" manufactured by Gulf Oil Corp.), polyacrylic acid emulsion ("Primal ASE-60" manufactured by Nihon Acryl Co., Ltd.), etc.

As the acid, there may be utilized various kinds of acids such as mineral acids (e.g. hydrochloric acid, hydrofluoric acid, sulfuric acid, phosphoric acid), organic acids (e.g. acetic acid) and their mixtures, provided that the effective and sufficient liberation of a metallic ion (e.g. Fe ion, Zn ion) from the surface of the metallic material can be assured in the aqueous composition. Particularly preferred is hydrofluoric acid.

The most preferred oxidizing agent is hydrogen peroxide. However, a variety of other oxidizing agents can be also used, for instance, chromium trioxide, potassium dichromate, potassium permanganate, potassium nitrate and ammonium persulfate. These oxidizing agents may be used alone or in combination.

The concentrations of the said essential components in the aqueous composition for coating are varied more or less with their kinds. In general, the aqueous coating composition includes about 5 to about 550 g./l. of polymer particles (i.e. resin solid), about 0.01 to about 0.50 g. equivalent/l. of the acid and about 0.01 to about 0.30 g. equivalent/l. of an oxidizing agent. A composition including 5 to 550 g./l. of polymer particles, 0.4 to 5.0 g./l. of fluoride ion and 0.3 to 3.0 g./l. of hydrogen peroxide is a typical example of suitable ones. It is preferred that such aqueous composition has a pH within the range of about 1.6 to about 5.0.

In addition to the said essential components, any water-dispersible pigment may be incorporated into the aqueous coating composition to provide a decorative effect upon and also to improve the corrosion resistance of the treated metallic surface. Examples of the pigment include phthalocyanine blue, phthalocyanine green, carbon black, iron oxide red, iron oxide yellow, quinacridone red, lead chromate, etc. Generally, these pigments provide excellent color variations not only with no sacrifice in coating quality but with, more often than not, enhancement of corrosion resistance. When a dry pigment is used, it is dispersed in the aqueous coating composition by a conventional procedure: e.g. the pigment is mixed with a small amount of a nonionic or anionic surface active agent and with some amount of water and dispersed by the aid of a high speed

mixer like Cowles Mixer, the said essential components are added to the resulting dispersion under further agitation and finally the bath solid content is adjusted by adding extra water thereto.

It is also possible to incorporate a coalescing agent into the aqueous coating composition in order that still further enhancement of corrosion resistance is realized. One of the most preferable coalescing agents is butyl cellosolve (i.e. ethyleneglycol monobutylether).

The method of this invention includes the steps of immersing a metallic surface as an anode and an appropriate electrode as a cathode in the aqueous coating composition set up in a bath and of applying a direct electric current through these electrodes. The bath voltage may be from about 2 to about 100 volts, preferably less than 50 volts. The immersion time is normally from about 5 to about 100 seconds, preferably less than 60 seconds. The thickness or weight of the resinous coating formed on the metallic surface from the immersion-electrolysis bath can be controlled by varying the time of applying an electric current and also by varying the voltage.

The application of direct electric current, i.e. passing a direct electric current through the aqueous coating composition is carried out as in the case of an ordinary electro-deposition coating. Nevertheless, the purpose of the application of electric energy is no more than the acceleration of the coating speed. For example, this procedure has nothing to do with the "throwing power" as defined in the electro-deposition coating but the throwing performance is solely dependent upon the behaviors of the essential components, i.e., the film-forming polymer, the acid and the oxidizing agent, in the aqueous coating composition.

The use of the same aqueous coating composition as above without application of any electricity can result in the formation of coating on the surface of a metallic material. In order to make a sufficient film thickness, however, it takes a long time. The application of a direct electric current according to this invention can shorten such time markedly.

Although a higher bath voltage over the said upper limit is operable and can form a good film, it is not advantageous from the economical viewpoint. Such a high voltage as around 150 volts or more is rather harmful because the rupture of the film will occur.

After the formation of coating is completed, the coated surface is withdrawn from the aqueous coating composition and baked usually at about 120 to about 250° C. for about 5 to about 30 minutes, depending upon the fusion characteristics of the polymer (i.e. resin).

Practical and presently preferred embodiments of the present invention are illustratively shown in the following examples.

EXAMPLE 1

Component	
Styrene-butadiene copolymer emulsion ("Hycar LX 407" manufactured by Nihon Geon Co., Ltd., resin solid, 48%)	180 g.
Hydrogen peroxide	2 g.
Hydrofluoric acid	3 g.
Tap water	ml. To make 1000

Hycar LX 407 was diluted with water, and the dilution was admixed with hydrofluoric acid and hydrogen peroxide with a good agitation. A steel panel, previously cleaned in a conventional alkali metal silicate solution, was immersed in the above obtained composition, and a direct electric current was passed between the panel and the second electrode at 20 volts for 30 seconds. The panel was taken out and dried in an oven at 160 to 200° C. for 5 to 10 minutes. The coating thickness averaged 40 μ , and the film was smooth and uniform.

EXAMPLES 2-8

The coating of a steel panel was carried out in the same manner as in Example 1 but using a different coating

composition. The thickness of the film thus formed on the surface of the panel is shown in Table 1.

TABLE 1

Ex. No.	Resin emulsion used	Resin emulsion (g./l.)	HF (g./l.) ¹	H ₂ O ₂ (g./l.) ²	Film thickness (μ)
2	Styrene-butadiene copolymer emulsion—("Pliolite 491" manufactured by Goodyear Rubber & Chemical Corp.; resin solid, 56 percent).	100	2 (0.1)	1.5 (0.09)	25
3	Acrylic copolymer emulsion ("Hycar LX 814" manufactured by Nihon Geon Co., Ltd.; resin solid, 48%).	100	2 (0.1)	1.5 (0.09)	27
4	Acrylic copolymer emulsion ("Hycar 2600 x 138" manufactured by Nihon Geon Co., Ltd.; resin solid, 48%).	100	2 (0.1)	1.5 (0.09)	27
5	Acrylic copolymer emulsion ("Polysol AP-300" manufactured by Kobunshi Kagaku Kogyo Co., Ltd.; resin solid, 48%).	100	2 (0.1)	1.5 (0.09)	24
6	Ethylene-vinyl acetate copolymer emulsion ("Polysol EVA-P-1" manufactured by Kobunshi Kagaku Kogyo Co., Ltd.; resin solid, 50%).	200	3 (0.15)	2 (0.11)	3
7	Polyethylene emulsion ("Poly-em 40" manufactured by Gulf Oil Corp.; resin solid, 40%).	150	2 (0.1)	1.5 (0.09)	2
8	Polyacrylic acid emulsion ("Primal ASE-60" manufactured by Nihon Acryl Co., Ltd.; resin solid, 30%).	400	1 (0.05)	1 (0.06)	60

¹ ² The numerals in parenthesis indicate the corresponding values by g. equivalent/l.

³ Since Primal ASE-60 performed as a film forming material and also as an acid, the amount of hydrofluoric acid was able to be reduced.

EXAMPLES 9-12

The coating of a steel panel was carried out in the same manner as in Example 1 but using a coating composition comprising Hycar LX 407 (180 g.), hydrogen peroxide (2 g.; 0.11 g. equivalent/l.) and an acid (as shown in Table 2) in tap water (to make 1000 ml.). The thickness of the film thus formed on the surface of the panel is shown in Table 2.

TABLE 2

Example number	Acid used	Amount of acid (g./l.) ¹	Film thickness (μ)
9	Hydrochloric acid	1 (0.03)	60
10	Sulfuric acid	3 (0.06)	28
11	Phosphoric acid	2 (0.06)	30
12	Acetic acid	20 (0.33)	20

¹ The numerals in parenthesis indicate the corresponding values by g. equivalent/l.

EXAMPLES 13-17

The coating of a steel panel was carried out in the same manner as in Example 1 but using a coating composition comprising Hycar LX 407 (180 g.), hydrofluoric acid (3 g.; 0.15 g. equivalent/l.) and an oxidizing agent (as shown in Table 3) in tap water (to make 1000 ml.). The thickness of the film thus formed on the surface of the panel is shown in Table 3.

TABLE 3

Example number	Oxidizing agent used	Amount of oxidizing agent (g./l.)	Film thickness (μ)	
13.....	Potassium dichromate....	3.5 (0.07)	35	5
14.....	Potassium permanganate..	2 (0.06)	15	
15.....	Sodium nitrate.....	2 (0.05)	60	10
16.....	Ammonium persulfate....	2 (0.02)	40	
17.....	{Chromium trioxide.....}	1 (0.03)	12	
	{Calcium carbonate.....}	0.2		15

EXAMPLE 18

Component		
Hycar LX 407	g.	180
Lead chromate 5G	g.	95
Anionic surface active agent ("Demol-P" manufactured by Kao-Atlas Co., Ltd.; resin solid, 30%)	g.	5
Hydrofluoric acid	g.	3.5
Hydrogen peroxide	g.	2.5
Tap water	ml.	To make 1000

Lead chromate, Demol-P and tap water were mixed together in a porcelain mill, and the mixture was milled for 16 hours. Then, Hycar LX 407 was admixed with hydrofluoric acid and hydrogen peroxide with a good agitation, and the resulting mixture is admixed with the above prepared color paste. A steel panel, previously cleaned in a conventional alkali metal silicate solution, was immersed in the above obtained composition, and a direct electric current was passed between the panel and the second electrode at 2.5 to 25 volts for 15 to 60 seconds. The panel was taken out and dried in an oven at 170° C. for 5 minutes. The thickness of the film thus formed on the surface of the panel is shown in Table 4.

TABLE 4

Immersion time (sec.)	Voltage (v.)	Film thickness (μ)
15.....	15	36
	20	45
	25	60
30.....	5	33
	10	49
	15	62
	20	73
	25	85
60.....	2.5	28
	5	52
	10	78
	15	100

¹³ In these cases, very uniform and smooth coatings were given.

EXAMPLES 19-21

The coating of a steel panel was carried out in the same manner as in Example 18 but using a different coating composition while passing a direct electric current at 20 volts for 30 seconds. The thickness of the film thus formed on the surface of the panel is shown in Table 5.

TABLE 5

Example number	Resin emulsion	Pigment	Surfactant	HF	H ₂ O ₂	Other	Film thickness (μ)
19.....	Hycar LX 407 (180)...	Lead chromate 5G (95)...	Demol-P (5).....	3.5	2.5	Butyl cellosolve (20)...	40
20.....	do.....	Phthalocyanin green (55)...	Nonionic surface active agent ("Emulgen A-60" manufactured by Kao-Atlas Co., Ltd.; resin solid, 98%) (3)...	3.5	2.5	60
21.....	Hycar LX 814 (220)...	Iron oxide red (50).....	Demol-P (2.5).....	4.5	3	29

In order to demonstrate the enhanced coating rate and the improved corrosion resistance according to the present invention, the comparison test was carried out using the aqueous coating compositions described in Examples 18 and 19 and adopting the coating conditions shown in

Table 6 with or without passing a direct electric current. The film appearance and thickness formed on clean steel panels are shown in Tables 6 and 7.

TABLE 6

Coating composition used	Immersion time (sec.)	Voltage (v.)	Film appearance ¹	Film thickness (μ)
Example:				
18.....	30	5	Excellent....	33
18.....	30	Fair.....	10
18.....	180	Excellent....	34
19.....	30	15	do.....	29
19.....	30	Bad.....	7
19.....	300	Good.....	25

¹ Film appearance was evaluated by the degree of surface uniformity and smoothness.

TABLE 7

Coating composition used	Salt spray test ¹	Impact test ²	Cross-hatch test ³
Example 18.....	{Rust: Some along the scribes....} {Blister: 3 mm. in width along the scribes.	No failure....	None.
Do.....	{Rust: Prominent along the scribes. {Blister: Moderate all over.....	do.....	Do.
Do.....	{Rust: Some along the scribes. {Blister: 2 mm. in width along the scribes.	do.....	Do.
Example 19.....	{Rust: Slight along the scribes.... {Blister: slightest.....	do.....	Do.
Do.....	{Rust: Prominent along the scribes. {Blister: Dotted all over.....	do.....	Do.
Do.....	{Rust: Some along the scribes. {Blister: Very few.....	do.....	Do.

¹ The test was carried out according to ASTM B-117-61 (90 hours).

² Du Pont Impact Tester was used. The test panel was impacted by a balling $\frac{1}{2}$ " ball with 1,000 g. weight from 50 cm. height, deforming the specimen.

³ The paint surface was scribed with parallel lines approximately 1 mm. apart and cut through to bare metal. Duplicate lines were scribed at right angles to make a cross-hatch pattern. Scotch brand cellophane tape was pressed smoothly over the scribed area. After several seconds, the tape was pulled back rapidly so that the tape was turned back upon itself approximately 180° from its original pressed position. The results are shown in the degree of failure noted; e.g. none, slight, moderate or heavy loss of paint.

What is claimed is:

1. A method for coating the surface of a metallic material which comprises immersing the metallic surface in an aqueous composition comprising a dispersion of a film-forming polymer, an acid, and an oxidizing agent, passing a direct electric current between the metallic surface and a secondary electrode, such that the metallic surface is anodic and the secondary electrode is cathodic and withdrawing the thus-coated metallic surface from the aqueous composition followed by baking the coated surface.

2. The method according to claim 1, wherein the metallic material is a ferriferous or zinciferous one.

3. The method according to claim 1, wherein the pH of the aqueous composition is within a range of about 1.6 to about 5.0.

4. The method according to claim 1, wherein the film-forming polymer is present in an amount within a range of about 5 to about 550 g. per liter of the aqueous composition.

5. The method according to claim 1, wherein the acid is present in an amount within a range of about 0.01 to about 0.50 g. equivalent per liter of the aqueous composition.

6. The method according to claim 1, wherein the oxidizing agent is present in an amount within a range of about 0.01 to about 0.30 g. equivalent per liter of the aqueous composition.

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7. The method according to claim 1, wherein the film-forming polymer is styrene-butadiene copolymer, acrylic copolymer, ethylene-vinyl acetate copolymer, polyethylene or polyacrylic acid.

8. The method according to claim 1, wherein the acid is hydrofluoric acid, hydrochloric acid, sulfuric acid, phosphoric acid or acetic acid.

9. The method according to claim 1, wherein the oxidizing agent is hydrogen peroxide, chromium trioxide, potassium dichromate, potassium permanganate, sodium nitrate or ammonium persulfate.

10. The method according to claim 1, wherein the electric current is a voltage of from about 2 to about 100 volts.

11. The method according to claim 1, wherein the aqueous composition contains a water-dispersible pigment.

12. The method according to claim 1, wherein the aqueous composition contains a coalescing agent.

13. A metallic material coated by the process of claim 1.

14. A method for coating the surface of a ferri-ferrous or zinciferous material which comprises immersing the surface in an aqueous composition of a dispersion of a film-forming polymer having a pH of from about 1.6 to about 5.0 and comprising from about 0.01 to about 0.50 g. equivalent/l. of an acid selected from the group consisting

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of hydrofluoric acid, hydrochloric acid, sulfuric acid, phosphoric acid and acetic acid and from about 0.01 to about 0.30 g. equivalent/l. of an oxidizing agent selected from the group consisting of hydrogen peroxide, chromium trioxide, potassium dichromate, potassium permanganate, sodium nitrate and ammonium persulfate, the film-forming polymer being contained in a concentration of from about 5 to about 550 g./l., said film-forming polymer being one selected from the group consisting of a styrene-butadiene copolymer, an acrylic copolymer, an ethylene-vinyl acetate copolymer, a polyethylene and a polyacrylic acid, passing a direct electric current of from about 2 to about 100 volts between the metallic surface and a secondary electrode, such that the metallic surface is anodic and the secondary electrode is cathodic and withdrawing the thus-coated metallic surface from the aqueous composition followed by baking.

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