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3,350,285

METHOD OF FORMING RUST-PROOFING AND CORROSION-RESISTING COATING ON METAL SURFACES

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5 Claims. (Cl. 204—56)

ABSTRACT OF THE DISCLOSURE

A rust-proof and corrosion-resistant film is provided on a metal surface by immersing the metal surface in an aqueous solution containing 0.005 to 1.0 weight percent of beryllium ion, 0.01 to 30 weight percent of chromium VI ion, and 0.01 to 5.0 weight percent of a high molecular weight compound such as polyvinyl alcohol, the solution having a pH of 3.0 to 6.0. The coating may be applied by a dipping process or by an electrolytic process utilizing the metal surface as a cathode.

Hitherto, as rust-proofing treatments of surfaces of all metals or metal parts of machines and tools including household utensils to precision instruments and machines, various processes have been developed and desirable effects have been attained in respective case. Also, as corrosion-resisting treatments of metal films formed on the surface of ceramics, glasses, synthetic resin articles, fibers, papers, cellophanes by a chemical plating method, spraying method, vacuum depositing method or adhesion method, such processes as coating protective film or applying protective material have been mainly used. However, these processes were not perfect as the film did not firmly adhere and there occur pin holes which cause corrosion after use for a certain time since the rust-proofing and heat-resisting properties are weak and the coated film is liable to be stripped when used frequently or exposed to high temperature as the film is not heat resistant. For instance, a gilt or silver thread has been produced by depositing the metal for a few millimicrons to a few microns on the synthetic resin film such as polyester, polycarbonate or polyethylene, and similarly on the papers, fabrics and cellophanes. But the product is soon discolored and deteriorated and since the deposited metal film is very thin it is liable to be stripped or dissolved easily if it makes contact with hot water or chemicals so that it has been protected by coating transparent synthetic resin but it has disadvantage that sufficient protection can not be assured. Furthermore, there are no appropriate methods for protecting thin film of metal deposited or spattered on glass, ceramics and organic articles.

The principal object of the invention is to obviate the above disadvantages and to provide protective coating on the surface of metal or metal film having excellent anti-corrosive and heat resistance which can be tightly and easily applicable at a lower cost without spoiling appearance, thereby improving anti-corrosive property of a metal and metal films.

Another object of the invention is to protect a metallized thin film formed on the surface of a phenol resin, epoxy resin, melamine resin, fluorine resin, polyester resin, used for printed wiring, etc. to prevent discoloration by formalin or other gases as well as to remarkably improve the durability and enables it to be used for electric purposes as the electric resistance is low.

A further object of the invention is to strengthen the

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metallized film by the inorganic material and to increase the resistance of the metallized film to several or several ten times of a conventional one and to improve the properties.

In carrying out the method of the invention in one way, the metal to be treated is dipped in a solution of beryllium salts containing one or more of chromates or bichromates as well as polyvinyl alcohol and the pH-value of which is adjusted to 3.0 to 5.0 or electrolyzed in said mixed solution using the metal as a cathode to form anti-corrosive film containing beryllium oxide, chromium oxide and organic substance on the surface of the metal.

In another embodiment of the invention, an aqueous solution is first prepared by adding a beryllium salt, one or more of chromates and bichromates, and if necessary, one or more of water-soluble organic materials and after adjusting the pH of the solution, a metal film is immersed in the aqueous solution and direct current is passed between the metal surface as a cathode and an anti-corrosive conducting material such as a lead plate or beryllium metal as anode to perform a weak electrolysis treatment.

In a further embodiment of the invention a mixed solution containing a water soluble inorganic salt that forms hydroxide at about neutrality and chromic acid or chromate ion added with a water soluble organic high molecular compound and a nonionic surface active agent is used for treating a metal and synthetic resins.

Polyvinyl alcohol used in the process of the invention prevents the formation of very small pin holes or cracks on the film depending on the kinds of metal. This is based on the fact that the addition of organic substances covers pin holes and cracks and can provide a film of uniform and good anti-corrosive property.

It is believed that this phenomenon results from the formation of film which is deposited from a complex compound formed by hydroxyl group of polyvinyl alcohol with beryllium. The film obtained according to the invention is colored from blue to yellowish gray, and has excellent anti-corrosive property and at the same time only slight amount of heat-cured polyvinyl alcohol is adhered on the surface treated so that the film is characterized by its good adhering and coating property.

As the beryllium salts are used inorganic and organic beryllium salts, such as, beryllium sulfate, beryllium hydroxide, beryllium nitrate, beryllium halide, basic beryllium acetate, beryllium chloride, beryllium citrate, and sodium fluoro beryllate. As chromates are used chromic anhydride and sodium chromate, and as bichromates are used sodium bichromate and potassium bichromate.

As water-soluble organic high molecular weight compounds are used polyvinyl alcohols, polyacrylic acid, polyethylene oxide, sucrose and furfural alcohols. A suitable concentration of Be ion in the solution is 0.005–1.0 weight percent, that of Cr (VI) ion is 0.01–30 weight percent, and that of the water-soluble organic substance is 0.01–5.0 weight percent. If their contents are lower than the above range, the rust-proofing power is low and if higher, the rust-proofing activity does not increase any further so that it is uneconomical.

Further, by adding less than about 5 weight percent of a nonionic surfactant or a reducing agent to the treating solution having the above composition, a uniform film having more excellent property can be obtained. As the nonionic surface active agent are effectively used triethanolamine; coconut amine and stearylpropylenediamine, and the like ethylene oxide derivatives; alkanolamines; alkanol- or phenolether-type derivative. They improve the properties of the film by causing a catalytic action and a surface active action on the surface of the metal.

Furthermore, by adding, as the reducing agent, an organic reducing agent having an aldehyde group or forming an aldehyde group during reaction, such as, sucrose, glucose, vanilin, and hexamethylene tetramine, and an inorganic reducing agent giving no harmful influences, the cathodic reduction is accelerated and in a dipping process insoluble chromates are precipitated, thereby improving rust-proofing effect.

Then, as to the influence due to the pH-value of the above mentioned mixed aqueous solution, a good result is obtained by adjusting the pH of the solution to 3-6. If the pH is above 6.0, a part of the solution is subjected to hydrolysis, which makes the treatment difficult, and if the pH is below 3, the rust-proofing effect is lowered.

Then, as to the influences due to the pH-value of the ture but the optimum temperature depends on the nature of metals to be treated. When a film coated on a glass, ceramics and organic article is treated a temperature lower than 30° C. is desirable, and at a higher temperature there occur more pin holes and frequent stripping of metal film. When a common metal is treated better rust-proofing coating can be obtained by treating with a solution heated to 40-70° C., whilst at a higher temperature the evaporation of liquid increases and organic substance is liable to be decomposed, thereby making the control of liquid, and lowering the rust-proofing property.

A nonionic surface active agent such as polyhydric alcohols or amines having the side chains of polyoxyethylene forms a stable chelate compound with Be while the hydrophilic group is adsorbed on the surface of the metal to be treated, whereby a uniform film having good adhesive property is formed.

Simultaneously, the hexa-valent chromium is partially reduced to tri-valent chromium during the drying step whereby a film having more excellent corrosion-resistance can be formed. The film formed by the method of the invention is a transparent precise film having 0.01-0.2 μ in thickness, the rust-proofing property of the film is very excellent, and the film can prevent rusting and stripping of the metal film even in steam, sodium sulfide, hydrogen sulfide, ammonia, sulfur dioxide gas, corrosive gases or liquids without spoiling the appearance of the metal. Further, by the process of the invention, a film having heat resistance up to 250-400° C. and very low contact resistance can be obtained, which can therefore serve as electric uses.

An article to be treated may be immersed in the above mentioned mixed solution after adjusting the pH to 3-6. Or, the solution may be sprayed on the article, or further, the article may be treated electrolytically in the solution by using the article as a cathode and a conductive material as an anode.

The electrolysis may be sufficiently carried out for 1 sec. to 20 min., most preferably at 5 min., at a current density of 0.01-5.0 amp/sq. dm. If the electrolysis is carried out at the conditions beyond the limit, the corrosion resistance is lowered, pin holes are formed on the metallized surface, or the metallized surface is stripped.

The electric current for the electrolysis may be a direct current, but in order to reduce the formation of pin holes without injuring the metallized film, it is preferable to use pulsating current or pulse current.

The film forming mechanism by the process of the invention is not clear, but as the results of electrochemical and analytical investigations about the film done by the inventors it is considered that according to the reduction of the H⁺ concentration caused by electrochemical action on the surface of the metal to be treated the metal ion forms colloidal hydrated ion, which is reduced and deposited on the metal surface to be treated together with the reduced chromic acid and the coated film, when dried, forms a film consisting of composite oxides of beryllium and chromium.

By adding the water-soluble organic resin the formation of pin holes between the inorganic film and the metal

surface to be treated is prevented to strengthen the mutual bonding to improve the adhesivity to the metallized surface and at the resin coating.

Further, in the case of using a polyhydric alcohol such as polyvinyl alcohol, a very beautiful film can be obtained since the alcohol forms a chelate compound with an element, e.g., beryllium which deposits on the cathode.

The invention will be explained further in detail by examples.

Example 1

Beryllium sulfate	-----g./l---	6.0
Chromic anhydride	-----g./l---	6.0
Potassium bichromate	-----g./l---	2.0
Polyvinyl alcohol	-----g./l---	5.0
pH (adjusted by a caustic soda solution)	-----	4.0
Temperature of treating solution	-----° C---	60

An article to be treated, that is an alumina porcelain or beryllia porcelain article metallized with copper was immersed for 5 seconds in the treating solution having the above composition, washed with water, and dried at 120° C. for 5 minutes to form a transparent film of 0.05 μ in thickness. When the sample applied with this treatment was placed in ammonia gas for 2 hours, in hydrogen sulfide gas for 2 hours and in spraying of an aqueous sodium chloride solution for 38 hours, no change was found. On the other hand, when a sample without being applied with this treatment was in the same conditions, the metallized portion was discolored and the metal film was stripped.

Example 2

Beryllium sulfate	-----g./l---	3.0
Chromic anhydride	-----g./l---	2.0
Triethanol amine	-----g./l---	0.5
pH (adjusted by caustic soda)	-----	5.0

In the above treating solution, an electrolytic treatment was carried out by using a lead plate as an anode and a mirror surface prepared by depositing silver on a glass surface by reduction as a cathode for 5 minutes with D.C. of 0.03 amp/sq. dm. and a transparent precise film of 0.1 μ was obtained. When the silver film treated with the process of the invention was exposed in hydrogen sulfide gas for 4 hours, there were no changes and when it was boiled in water for 24 hours, no substantial stripping of the film occurred.

On the other hand, the same but untreated silver film changed in hydrogen sulfide gas into black in 2 minutes and all the film was stripped when it was placed in boiling water for 4-5 hours.

Example 3

Beryllium hydroxide	-----g./l---	1.5
Sodium bichromate	-----g./l---	3.0
Polyethylene oxide	-----g./l---	3.0
pH	-----	5.5
Temperature of treating solution	-----° C---	20

An epoxy resin was coated on a film obtained by carrying out the electrolytic treatment in the above treating solution for 1 minute at D.C. of 0.1 amp/sq. dm. by using a lead plate as an anode and a mirror surface prepared by depositing silver on a glass as a cathode. When thus treated mirror was exposed in hydrogen sulfide gas for 15 hours and in steam (100° C.) for 4 days, no changes were perceived.

On the other hand, the silver surface on which only the epoxy resin was coated swelled within the above period and from the portion, the metal film discolored and was stripped.

Example 4

Beryllium hydroxide	-----g./l---	3.7
Chromic anhydride	-----g./l---	2.0
Temperature of treating solution	-----° C---	15

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In the above treating solution, an electrolytic treatment was carried out by using a lead plate as an anode and a mirror surface prepared by depositing silver on a glass surface by reduction as a cathode for 3 minutes with rectified pulse current of 0.1 amp/sq. dm. (passed for 0.5 sec. rested for 0.5 sec.) and a film thus obtained was exposed in hydrogen sulfide gas atmosphere for 10 hours, but there were no changes.

Example 5

Beryllium sulfate	g./l.	3
Chromic anhydride	g./l.	2
Polyvinyl alcohol	g./l.	5
Nonionic surface active agent	g./l.	0.05
pH		5.5
Temperature of treating solution	° C.	5

In the above treating solution was immersed as a cathode a polyester film vacuum deposited with aluminum and the electrolysis was carried out under the following conditions:

Rectified pulse current	passed for 0.5 sec., rested for 0.4 sec.
Maximum current density	0.4 amp/sq. dm.
Pulse times	15 repetitions.

After the electrolytic treatment, the film was washed with water and dried for 5 minutes at 100° C.

Example 6

Beryllium sulfate	g./l.	5
Sodium bichromate	g./l.	7
Polyvinyl alcohol	g./l.	2
Nonionic surface active agent	g./l.	0.1
pH		5.7
Temperature of treating solution	° C.	10

A polycarbonate film vacuum deposited with aluminum was immersed as a cathode in the solution and the polycarbonate film as an anode and electrolyzed under the following condition:

Direct current:	
Electrolysis time	sec. 10
Current density	amp/sq. dm. 0.1

The film, after the treatment, was washed with water and dried for 3 minutes at 120° C.

Example 7

Beryllium sulfate	g./l.	5
Aluminum sulfate	g./l.	5
Chromic anhydride	g./l.	2
Polyacrylic acid	g./l.	3
Nonionic surfactant	g./l.	0.01
pH		5.0
Temperature of treating solution	° C.	20

A polyester film vacuum deposited with aluminum was immersed in the solution having the above conditions and electrolyzed as a cathode with a lead plate as an anode under the following electrolytic condition:

Rectified pulse current	passed for 0.7 sec. rested for 0.5 sec.
Current density	0.8 amp/sq. dm.
Pulse time	10 repetitions.

After the electrolytic treatment, the film was washed with water and dried for 5 minutes at 100° C.

Example 8

Beryllium hydroxide	g./l.	1.5
Chromic anhydride	g./l.	3
Polyvinyl alcohol	g./l.	7
Nonionic surfactant		Slight
pH		5.0
Temperature of treating solution	° C.	10

A polyester film vacuum deposited with silver was immersed in the solution having the above conditions and

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electrolyzed as a cathode with a lead plate as an anode under the following electrolytic conditions:

Rectified pulse current	Passed for 0.3 sec., rested for 0.5 sec.
Current density	0.5 amp/sq. dm.
Pulse times	30 repetitions.

After the electrolytic treatment, the film was washed with water and dried for 5 minutes at 80° C.

Example 9

Beryllium sulfate	1 part (as Be).
Nickel sulfate	1 part (as Ni).
Chromic anhydride	10 parts (as Cr).
Polyvinyl alcohol	20 parts.
pH	5.5.
Temperature of treating solution	20° C.

A phenol resin plate applied with a print wiring of copper was immersed in the solution having the above conditions and electrolyzed high metallized portion as a cathode and a lead plate as an anode under the following conditions:

Direct current:	
Electrolysis	min. 1
Current density	Amp/sq. dm. 0.03

After the electrolysis, the plate was washed with water and dried for 3 minutes at 100° C.

Example 10

Beryllium sulfate	g./l.	2
Chromic anhydride	g./l.	5
Nonionic surfactant	g./l.	0.5
pH		3.5
Temperature of treating solution	° C.	15

In the solution having the above conditions was immersed a cellophane film deposited with copper and electrolyzed with the cellophane film as a cathode and a lead plate as an anode under the following electrolytic conditions:

Rectified pulse current	Passed for 0.3 sec., rested for 0.5 sec.
Current passing time	2 minutes.
Current density	0.4 amp/sq. dm.

After the electrolytic treatment, the film was simply washed with water and dried for 3 minutes at 100° C.

Example 11

Beryllium sulfate (as Be)	parts. 1
Aluminum ammonium sulfate (as Al)	do. 0.5
Sodium bichromate (as Cr)	do. 15
Polyvinyl alcohol	do. 20
Nonionic surface active agent	Slight
pH	3.5
Temperature of treating solution	° C. 20

A cotton cloth vacuum deposited with aluminum was immersed in the solution having the above conditions for 51 seconds, withdrawn, then washed with water and dried for 5 minutes at 120° C.

About the samples treated in Examples 5 to 11 were applied the following tests; that is, a boiling water test (immersed for 1 hour in boiling water at 100° C.); a formic acid test (immersed for 30 minutes in an aqueous 0.5% formic acid solution at 60° C.); and oxalic acid test (immersed for 30 minutes in an aqueous 0.35% oxalic acid solution at 100° C.); a silk-refining test (immersed for 30 minutes at 100° C. in an aqueous solution containing 4.2 g./l. of solid soap, 6 cc./l. of sodium silicate and 0.9 g./l. of hydrosulfide); a hydrogen sulfide test (exposed in hydrogen sulfide stream for 30 minutes); and a formalin test (exposed on a formalin solution for 24 hours).

The results are shown in the following table.

TABLE 1

	Boiling water test	Formic acid test	Silk- refining test	Hydrogen sulfide test	Oxalic acid test	Forma- lin test
Untreated deposited film Al.....	X	X	X	-----	X	-----
Untreated deposited film Cu.....	X	-----	-----	X	-----	X
Untreated deposited film Ag.....	X	-----	-----	X	-----	X
Example 5.....	O	O	O	-----	O	-----
Example 6.....	O	O	Δ	-----	O	-----
Example 7.....	O	Δ	Δ	-----	O	-----
Example 8.....	O	O	-----	O	-----	-----
Example 9.....	-----	-----	-----	O	-----	O
Example 10.....	O	-----	-----	O	-----	O
Example 11.....	Δ	Δ	Δ	-----	Δ	-----

O=Unchanged; Δ=Changed a little; X=Corroded.

Example 12

Beryllium sulfate -----g./l. 15
 Chromic anhydride -----g./l. 5
 Polyvinyl alcohol -----g./l. 5
 pH ----- 5.0
 Temperature of treating solution -----°C. 60

A mild steel plate was electrolyzed for 1 minute at 0.2 amp/sq. dm. in said solution and dried for 5 minutes at 150° C. to form a film according to the present process. The sample applied with the present treatment did not produce red rust for 75 hours on Salt Water Spray Test according to JIS Z-2371 specification.

Example 13

Beryllium hydroxide -----g./l. 3.5
 Chromic anhydride -----g./l. 5
 Polyvinyl alcohol -----g./l. 10
 pH ----- 5.0
 Temperature of treating solution -----°C. 40

A mild steel plate was electrolyzed for 1 minute; was treated by electrolysis according to the above example, untreated steel plate (a), commercial product which was treated by cathode-electrolysis according to known phosphoric acid solution (b) were compared on test. The result is shown in Table 2 below.

TABLE 2.—SALT WATER SPRAY TEST ACCORDING TO JIS Z-2371 SPECIFICATION

Sample.....	Rate of rust creation		
	a, percent	b, percent	Product according to the invention, percent
Spray time (hr.):			
1.....	8	0	0
10.....	12	6	0
20.....	70	40	0
30.....	100	85	0
50.....	100	100	0
100.....	100	100	5

Example 14

Beryllium sulfate -----g./l. 6
 Potassium bichromate -----g./l. 5
 Polyvinyl alcohol -----g./l. 5
 pH ----- 4.0
 Temperature of treating solution -----°C. 60

A zinc plate was dipped for 10 seconds in said solution, the liquid was squeezed with a roll and the plate was dried for 5 minutes at 150° C.

The results obtained by dipping the plates according to

above examples are shown in Table 3 by taking the untreated zinc plate as (c) for comparison.

TABLE 3.—SALT WATER SPRAY TEST ACCORDING TO JIS Z-2371 SPECIFICATION

Sample.....	Rate of rust creation	
	c, percent	Product according to the invention, percent
Spray time (hr.):		
5.....	0	0
10.....	10	0
30.....	100	0
60.....	100	0
90.....	100	0
120.....	100	5
150.....	100	7

What we claim is:

1. A method of forming rust-proof and corrosion-resistant coatings on a metal film secured to a base, which comprises dipping said metal film in an aqueous solution consisting essentially of water, a beryllium salt selected from the group consisting of beryllium hydroxide, beryllium sulfate, beryllium nitrate, beryllium halide, basic beryllium acetate, beryllium citrate, sodium fluoro beryllate and potassium fluoro beryllate in the range from 0.005 to 1.0 weight percent as beryllium ion concentration, at least one compound selected from the group consisting of chromic anhydride, chromate, and bichromate in the range from 0.01 to 30 weight percent as chromium (VI) ion concentration, and a water soluble organic high molecular compound selected from the group consisting of polyvinyl alcohol, furfural alcohol, polyethylene oxide, and polyacrylic acid in the range from 0.01 to 5.0 weight percent, regulating the pH of said solution in the range of 3.0 to 6.0, and passing an electric current having a density of 0.01 to 5.0 amp/dm.² through said solution employing said metal film as a cathode.

2. A method according to claim 1, wherein said solution contains less than 5 weight percent of wetting agents.

3. A method according to claim 1, wherein said solution contains less than 5 weight percent of reducing agents.

4. A method according to claim 1, wherein a part of beryllium ion in said treating solution, which is the essential ingredient, is replaced with at least one ion of a metal selected from the group consisting of aluminum, nickel and cobalt.

5. An aqueous solution for forming a rust-proof and corrosion resistant coating on the surface of a metal film which consists essentially of water, a beryllium salt selected from the group consisting of beryllium hydroxide,

beryllium sulfate, beryllium nitrate, beryllium halide, basic beryllium acetate, beryllium citrate, sodium fluoro beryllate and potassium fluoro beryllate in the range from 0.005 to 1.0 weight percent as beryllium ion concentration, at least one compound selected from the group consisting of chromic anhydride, chromate and bichromate in the range from 0.01 to 30 weight percent as chromium (VI) ion concentration, and a water soluble organic high molecular weight compound selected from the group consisting of polyvinyl alcohol, furfural alcohol, and polyethylene oxide, polyacrylic acid in the range from 0.01 to 5.0 weight percent, the pH of said solution being in the range of 3.0 to 6.0.

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CERTIFICATE OF CORRECTION

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Susumu Nishigaki et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 9, line 10, cancel "and"; line 11, after "oxide" insert -- , and --.

Signed and sealed this 30th day of December 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents