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3,519,542

PROCESS FOR TREATING A CATHODICALLY CHROMATED METAL SURFACE

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No Drawing. Filed Oct. 22, 1965, Ser. No. 502,277
Claims priority, application Japan, Nov. 12, 1964, 39/63,648

Int. Cl. C23f 7/26; C23b 11/00
U.S. Cl. 204—35

1 Claim

ABSTRACT OF THE DISCLOSURE

A process of improving cathodically produced hydrated chromium oxide coatings on metals comprises immersing at a temperature of 30° to 70° C. for a period of 1 to 60 seconds the coated metal in an aqueous solution of 1 to 50 gms./l. of at least one cationic surface active agent selected from the group consisting of aliphatic primary amine acetates, quaternary ammonium salts, pyridinium salts, picolinium salts, polyoxyethylene alkyl amines, and a composition selected from the group consisting of polycondensation products of dicyanodiamide and formaldehyde, dicyanodiamidine and formaldehyde, guanidine and formaldehyde, and diguanide and formaldehyde.

The present invention relates to a process for improving the properties of the coating formed in the cathodic chromating of metal surfaces.

Cathodic chromating is a process in which hexavalent chromium ions derived from chromic acid, chromates or dichromates in a treating solution are electrolytically reduced, mainly to trivalent state, to form a protective coating of a hydrated chromium oxide complex on the cathode metal. In the present specification the expression "hydrated chromium oxide coating" is employed to designate the film formed by chromating.

An analysis of the film formed shows that it contains no metals other than chromium, which is not present as simple metallic chromium. The analysis also shows that the film contains very little of the anion which was originally present in the chromating solution as an addition agent.

When the wetted hydrated chromium oxide coating formed is immediately dried at an appropriate temperature after the chromating, the anion in the coating is fixed as a member of a co-ordinated complex structure of the coating. In a wetted state, however, the anion is not firmly fixed in the structure and behaves as if it was physically absorbed.

As shown in the specific examples, the conditions for a cathodic chromating process are quite different from those for chromium plating, dip chromating and anodic chromating. A coating formed in chromium plating is simple metallic chromium and the coating formed by dip chromating is mainly a chromium chromate and in some cases is a mixture of a chromate and an oxide of the coated metal. The coating formed by anodic chromating is a mixture of a chromate and an oxide of the coated metal.

In the cathodic chromating process, various addition agents such as boric acid, phosphoric acid, sulfuric acid, disulfonic acid, nitric acid, acetic acid, or their respective salts and halogen compounds are added to the electrolyte, which mainly contains hexavalent chromium ion derived from chromic acid, chromates or dichromates as described in U.S. Pats. Nos. 2,733,199, 2,780,592, 2,769,774, 2,998,316 and 3,032,487.

Of these additive agents; such strongly acidic and cor-

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rosive anions as sulfate ion, nitrate ion or chlorate ion are concerned in electrolytic reduction of hexavalent chromium ion, and are physically adsorbed in the hydrated chromium oxide film on metal surface. The adsorbed anion in the film is water soluble and is dissolved out of the film under highly humid conditions to accelerate corrosion of cathodically chromated metal.

Consequently, the additive agent which gives a strongly acidic anion is necessary to form an excellent film in cathodic chromating but it has a detrimental effect to the corrosion resistance of the formed film. Therefore, the adsorbed anion should be thoroughly removed or should be surely restrained.

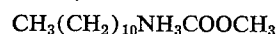
Furthermore, the sensitivity of the hydrated chromium oxide film to oil adsorption has also a detrimental effect to the lacquer adhesion, especially, in the case of direct lacquering after degreasing a lubricant on the film, because the adsorbed oil on the film is very difficult to be removed by conventional degreasing and causes poor adhesion. Accordingly, the sensitivity of the film to oil adsorption should be properly improved within the limit not to impair the original lacquer adhesion property.

In order to restrain the strongly acidic anion adsorbed in the hydrated chromium oxide film and to improve the adsorption property of the film, an immediate immersion of cathodically chromated metal in an aqueous solution containing at least one water-soluble or water-dispersible cationic surface active agent selected from the group consisting of aliphatic primary amine acetates, quaternary ammonium salts, pyridinium salts, picolinium salts, polyoxyethylene alkyl amines and polycondensation products obtained by the reaction of dicyandiamides and formaldehyde is most effective.

The following cationic surface active agents are used in the present invention.

(1) Aliphatic primary amine acetates.—Aliphatic primary amine acetates are the compounds having a formula of RNH_3COOCH_3 wherein R is an aliphatic hydrocarbon group having 8–18 carbon atoms, and showing cationic activity in water.

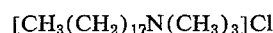
For example, undecylamine acetate



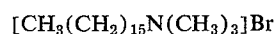
heptadecylamine acetate $CH_3(CH_2)_{16}NH_3COOCH_3$ and octadecylamine acetate $CH_3(CH_2)_{17}NH_3COOCH_3$.

(2) Quaternary ammonium salts.—Quaternary ammonium salts are the compounds having a formula of $[RRR'R''N]X$ wherein R is an alkyl group having 1–5 carbon atoms, R' is a member selected from the group consisting of saturated and unsaturated aliphatic hydrocarbon group having 1–22 carbon atoms, benzyl group and alkanol group having 1–5 carbon atoms, R'' is an aliphatic hydrocarbon group having 8–22 carbon atoms, X is halogen atom or hydroxyl group, and showing cationic activity in water, and also their derivatives having at least one ester bond, one ether bond or one amide bond in the molecules, and showing cationic activity in water.

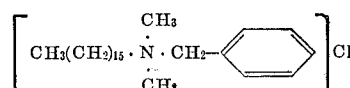
For example, trimethyloctadecyl ammonium chloride



trimethylcetyl ammonium bromide

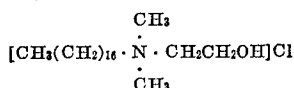


dimethylcetylbenzyl ammonium chloride

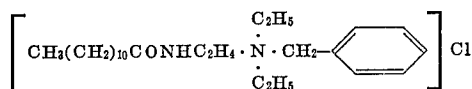


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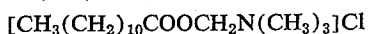
dimethylheptadecyl-2-hydroxyethyl ammonium chloride



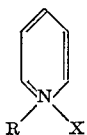
diethylbenzylauramidoethyl ammonium chloride



trimethyllauroyloxymethyl ammonium chloride

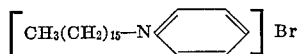


(3) Pyridinium salts.—Pyridinium salts are the compounds having a formula of

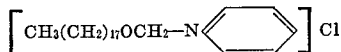


wherein R is an aliphatic hydrocarbon group having 12–18 carbon atoms, X is halogen atom, and showing cationic activity in water, and also their derivatives having at least one ester bond, one ether bond or one amide bond in the molecules and showing cationic activity in water.

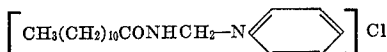
For example, cetylpyridinium bromide



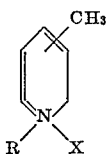
octadecyloxymethyl pyridinium chloride



lauramidomethyl pyridinium chloride

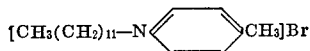


(4) Picolinium salts.—Picolinium salts are the compounds having a formula of

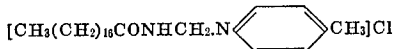


wherein R is an aliphatic hydrocarbon group having 12–18 carbon atoms, X is halogen atom, and showing cationic activity in water and also their derivatives having at least one ester bond, one ether bond or one amide bond in the molecules, and showing cationic activity in water.

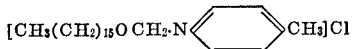
For example, lauryl picolinium bromide



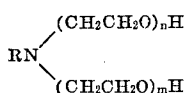
stearamidomethyl picolinium chloride



cetyloxymethyl picolinium chloride



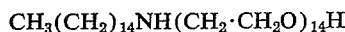
(5) Polyoxyethylene alkyl amines.—Polyoxyethylene alkyl amines are the compounds having a formula of



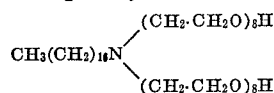
or $\text{RNH}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ wherein R is an aliphatic hydrocarbon group having 8–22 carbon atoms, n or m is a number of ethyleneoxide ($n, m=8-18$) and, showing cationic activity in water.

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For example, tetradecaoxyethylene pentadecylamine

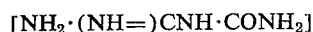


dioctaoyethylene heptadecylamine



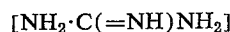
(6) Polycondensation product obtained by the reaction of dicyanodiamides and formaldehyde, and showing cationic activity in water.—For example, a polycondensation product of dicyanodiamide $[\text{NH}_2 \cdot (\text{NH}=\text{CNH}) \cdot \text{CN}]$ and formaldehyde $[\text{HCHO}]$.

A polycondensation product of dicyanodiamidine



and formaldehyde $[\text{HCHO}]$.

A polycondensation product of guanidine



and formaldehyde $[\text{HCHO}]$.

A polycondensation product of diguanidine



and formaldehyde $[\text{HCHO}]$.

These cationic surface active agents can be used alone or by mixture.

The treatment according to the present invention is effective for restraining an adsorbed anion in hydrated chromium oxide film to prevent a cathodically chromated metal from rusting under highly humid conditions.

The treatment is also suitable for increasing the lacquer adhesion effect on an cathodically chromated metal in all respects, and for improving the lacquer adhesion property, especially in the case of lacquer coating on the mechanically shaped metal after degreasing a lubricating oil.

In the treatment, cationic surface active agents above mentioned can easily adsorb an anion adsorbed in the hydrated chromium oxide film in wetted state and make a desirable barrier for oil adsorption.

The conditions required for performing the process described in the present invention will be summarized as follows:

- (1) Concentration of cationic surface active agent—1–50 g./liter
- (2) Temperature—30–70° C.
- (3) Dipping time—1–60 seconds

The optimum concentration of cationic surface active agent covers the range from 1 g./liter to 50 g./liter.

Generally, an increase of concentration results in an increase in an amount of cationic surface active agent to be adsorbed into the formed film. However, when the concentration of cationic surface active agent exceeds 50 g./liter, the hydrated chromium oxide film becomes bluish yellow and shows no more improvement.

When the concentration is less than 1 g./liter, the process needs longer treating time which is not practical for the short time of commercial operation.

An increase of temperature results in an increasing effect on the improvement, but in actual operation, a higher temperature increases an evaporation loss of water and an decomposition of cationic surface active agent. The operation should be preferably controlled at a temperature below 70° C.

On the other hand, a decrease temperature results in a decrease of an adsorbing power of cationic surface active agent into the formed film, and at a temperature below 30° C., the process requires an impracticably long treating time.

Therefore, it is preferable to conduct the operation in the temperature range of between 30° C. and 70° C.

An increase in dipping time results in an increase in an adsorbed amount of cationic surface active agent into the formed film, however, in the concentrations of treat-

ing solution of 1–50 g./liter and in the temperature range of 30–70° C., the dipping time of 1–60 seconds may be sufficiently effective for the improvement of corrosion resistance and lacquer adhesion property of the film.

When the dipping treatment is conducted in a very short time less than 1 second, the process requires higher concentration and higher temperature than those described above and it is practically impossible in commercial operation.

When the film formed in cathodic chromating is forced to dry, a dipping treatment in an aqueous solution containing cationic surface active agent is less effective because the dried film behaves as a hard barrier against the action of the surface active agent. Therefore, the treatment should be immediately performed in wetted state immediately after the forming of film by cathodic chromating.

The iron and steel sheets treated according to the present invention can withstand outdoor exposure tests for two months in winter and for 15 days in summer and also resist salt spray tests for 48 hours without any sign of rust.

They further resist humidity chamber tests in a relative humidity of 90% at 40° C. for one week without any sign of discoloration of the film.

Such a high corrosion resistance of coating as in the present invention has not heretofore been attained by conventional treatment.

After applying an about 10 micron film of modified alkyd or modified epoxy lacquer on steel sheet treated according to the present invention, the lacquered sheet was deeply drawn to make the cup with a drawing ratio of 2.2 and having a screw-shaped ridge on the cup wall to make a screw-shaped cup; when tested by adhesive tape, the lacquered side of the cup showed no peeling out.

In the case of lacquer coating on the mechanically shaped metal after degreasing a lubricating oil, superior lacquer adhesion was also found in the electrolytically chromated metal treated according to the present invention.

Other features of the lacquer adhesion property will be described in the following examples.

Metals treated according to the present invention showed good heat resistance up to 300° C., and weldability as good as the base metals.

As metals to be treated according to the present invention, the conventional metals to be treated in cathodic chromating under ordinary conditions, such as iron, steel, aluminum, chromium, nickel, zinc, tin, cadmium, magnesium, copper, titanium, their respective alloys and metals having the surface thereof are suitable.

The examples of the present invention are as follows:

EXAMPLE 1

A 0.25 mm. thick cold rolled low carbon steel sheet, the so-called black plate was cathodically cleaned for 20 seconds at a current density of 4 a./sq. dm. at 70° C. in a 7% sodium hydroxide solution, then rinsed with water, pickled for 10 seconds at room temperature in a 7% sulfuric acid, again rinsed with water and immediately treated cathodically using a lead antimony alloy anode under the following condition in the chromating solution of the following composition, immediately rinsed with water, and immediately dipped in the treating solution of the present invention under the condition given below, and again immediately rinsed with water and dried.

- (1) The electrolyte and the condition of cathodic chromating:

Chromic acid—50 g./liter
Sulfuric acid—0.2 g./liter
Hydrofluosilicic acid—0.3 g./liter
Temperature—50° C.
Electric current density—20 a./sq. dm.
Time—10 seconds

- (2) The treating condition of the present invention:

Trimethyloctadecyl ammonium chloride—50 g./liter
Dipping time—30 seconds

A transparent, bluish purple film was formed and the steel sheet thus treated showed very little rusty spots after being subjected to a salt spray test by a 5% sodium chloride solution for 48 hours at 35° C. and it showed no rusty spot and no discoloration when subjected to a humidity chamber test with a relative humidity of 90% for one week at 40° C.

EXAMPLE 2

A 0.5 mm. cold rolled low carbon steel sheet was subjected to the same pretreatment and the same cathodic chromating, as described in Example 1, and then immediately rinsed with water and immediately dipped in the treating solution of the present invention under the following condition and again immediately rinsed with water and dried.

- A polycondensation product between formaldehyde and dicyanodiamide—10 g./liter
Temperature—50° C.
Dipping time—2 seconds

The film formed was bluish yellow and transparent.

The steel sheet thus treated was applied with about 30 mg./sq. dm. of machine oil No. 120, degreased after 24 hours' standing still with trichloroethylene vapor for 2 minutes, then coated with about 20 microns of melamine modified alkyd enamel and subjected to a cross cut test which showed no peeling of the enamel was found.

Furthermore, after the steel ball having a diameter of 12.7 mm. and a weight of 500 g. was dropped from a height of 20 cm. on the enamel coated steel sheet surface thus treated, the impact part is tested by adhesive tape, and no adhesion loss of enamel was also found.

EXAMPLE 3

The same kind of cold rolled low carbon steel sheet as in Example 1 was subjected to the same pretreatment as described in Example 1, and then immediately treated cathodically using a lead antimony alloy anode under the following condition in the chromating solution of the following composition, again immediately rinsed with water and immediately dipped in the treating solution of the present invention under the following condition and again immediately rinsed with water and dried.

- (1) The electrolyte and the condition of cathodic chromating:

Chromic acid—60 g./liter
Phenol-2, 4-disulfonic acid—0.6 g./liter
Temperature—50° C.
Current density—20 a./sq. dm.
Time—20 seconds

- (2) The treating condition of the present invention:

Octadecylamine acetate—1 g./liter
Temperature—55° C.
Dipping time—60 seconds

The film formed was bluish yellow and transparent and the steel sheet thus treated was found to show almost no rusty spots when subjected to the same salt spray test as in Example 1 for 48 hours and when the steel sheet treated was coated with about 20 microns of melamine modified alkyd enamel and subjected to the same salt spray test as in Example 1 for 150 hours, no blister of the enamel was found.

EXAMPLE 4

The same kind of cold rolled low carbon steel sheet as described in Example 1 was subjected to the same pretreatment as described in Example 1 and then immediately treated cathodically using a lead antimony alloy anode under the following condition in the chromating solution of the following composition, again im-

mediately rinsed with water and immediately dipped in the treating solution of the present invention under the following condition and again immediately rinsed with water and dried.

- (1) The electrolyte and the condition of cathodic chromating:
- Sodium dichromate—500 g./liter
 - Chromium sulfate—10 g./liter
 - Ammonium sulfate—20 g./liter
 - Temperature—50° C.
 - Current density—25 a./sq. dm.
 - Time—8 seconds
- (2) The treating condition of the present invention:
- Cetyl pyridinium chloride—5 g./liter
 - Temperature—30° C.
 - Dipping time—20 seconds

A transparent, bluish purple film was formed and it had the similar corrosion resistance to those in Example 1.

EXAMPLE 5

The same kind of cold rolled low carbon steel sheet as described in Example 1 was subjected to the same pretreatment and the same cathodic chromating, as described in Example 1, and then immediately rinsed with water and immediately dipped in the treating solution of the present invention under the following condition and again immediately rinsed with water and dried.

Dimethyleylbenzyl ammonium chloride—10 g./liter
Di-octaoxyethylene stearylamine—10 g./liter
Temperature—70° C.
Dipping time—5 seconds

A transparent, yellowish and bluish purple film was formed. When the steel sheet thus treated was coated with about 10 microns of modified alkyd white enamel and deeply drawn to the cup with a drawing ratio of 2.2, no adhesion loss of the enamel was found on the cupwall. Furthermore, when the deeply drawn cup was immersed in a 3% boiling solution of sodium chloride for one hour, no adhesion loss was also found.

EXAMPLE 6

A 0.5 mm. aluminum sheet was cleaned for 10 seconds at room temperature in a 2% solution of sodium bicarbonate, rinsed with water and then immediately subjected to the same cathodic chromating as described in Example 1, then immediately rinsed with water and immediately dipped in the treating solution of the present invention under the following condition and again immediately rinsed with water and dried.

A polycondensation product between formaldehyde and dicyanodiamide—5 g./liter
Temperature—55° C.
Dipping time—20 seconds

The film formed was colorless and transparent, and when the aluminum sheet thus treated was subjected to a porosity test by cupric sulfate solution for two hours, no porosity was found.

EXAMPLE 7

A galvanized steel sheet with 0.15% aluminum was treated cathodically using a lead antimony alloy anode under the following condition in the chromating solution of the following composition and then immediately

rinsed with water and immediately dipped in the treating solution of the present invention under the following condition and again immediately rinsed with water and dried.

- (1) The electrolyte and the condition of cathodic chromating:
- Sodium dichromate—100 g./liter
 - Sulfuric acid—2 g./liter
 - Temperature—50° C.
 - Current density—5 a./sq. dm.
 - Time—1 second
- (2) The treating condition of the present invention:
- Trimethyloctadecyl ammonium chloride—30 g./liter
 - Temperature—50° C.
 - Dipping time—10 seconds

The formed film was colorless and transparent and when the galvanized steel sheet thus treated was coated with about 20 microns of melamine modified alkyd enamel and subjected to a cross cut test and an impact test, no adhesion loss of the enamel was found.

What we claim is:

1. A process for improving the corrosion resistance and reducing oil adsorption in a wet hydrated chromium oxide coating cathodically deposited on a cathode metal selected from the group consisting of iron and steel which comprises rinsing the wet chromated metal with water prior to drying, restraining entrapped anions selected from the group consisting of sulfate, nitrate and chlorate anions by immediately immersing said metal in an aqueous solution at a temperature of 30° to 70° C. for a period of 1 to 60 seconds containing from 1 to 50 grams per liter of at least one cationic surface active agent selected from the group consisting of polycondensation products of dicyanodiamide and formaldehyde, dicyanodiamidine and formaldehyde, guanidine and formaldehyde, and diguanide and formaldehyde rinsing the treated hydrated chromium oxide coating and drying the same.

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U.S. Cl. X.R.

106—14; 148—6.14, 6.2; 204—38, 56