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3,140,204

METHOD OF INACTIVATING METAL SURFACES

Schizuka Tokunaga, Kitatama-gun, Tokyo, Japan,
assignor to Nihon Parkerising Kabushiki Kaisha,
Tokyo, Japan, a corporation of Japan

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This invention relates to a method of inactivating metal surfaces which comprises treating said metal surfaces, or the inorganic films formed thereupon, with an acid aqueous solution of resins containing hexavalent chromium and a moistening and inhibiting agent. The object of this invention is to provide better inactivation of the surfaces of metallic materials, thereby facilitating adhesion of coatings to said surfaces.

Heretofore, the methods of producing chromate films, resinous films and the like upon metal surfaces by chemical or physical means, in order to protect the metal surfaces from corrosion or to obtain good preparation of metal surfaces on which coatings are to be applied, have been widely known. However, in the known methods of treating metal surfaces with an acid aqueous solution containing chromic acid, there was a defect in that the accompanying by-product of an trivalent chrome ion impaired the treating liquid, thereby reducing the effect of treatment. For this reason it is conventional for this kind of treating liquid to be used combiningly with a complex ion forming agent. However this method still does not completely protect the treating liquids from being impaired, and the management of the treating liquids becomes complicated.

Also, in the heretofore known method of treating metal surfaces with a solution of water soluble resins, wherein a treating liquid having 7-9.2 pH is used, the films formed do not adhere to the metal surfaces as strongly as is desired.

In another known method wherein a resinous aqueous solution containing hexavalent chromium is used for treatment, the treating liquid is either strongly acid, having 0.9-1.0 pH or neutral or weak alkali, having 7-9.2 pH. However, the treatment with a strong acid aqueous solution is defective in that it limits the metallic materials that can be treated and the inactivating film is deteriorated by the corrosion product which forms on the metal surface during the treatment. In the case of treating with a neutral or weak alkali aqueous solution, the action and effect of the contained chromic acid is not sufficient to attain the desired inactivation of the surfaces.

The objects of this invention are, by way of eliminating the above deficiencies of the heretofore known methods, to increase corrosion-resistance of treated products, improve adhesion of coatings and provide better finishes on the treated products by adding further gloss.

The effects of this inventive method are to improve the anti-corrosiveness of metal surfaces and the adhesiveness of coatings to said surfaces, at the same time providing a better appearance to the finished products, by means of inactivating metal surfaces by forming on said surfaces a smooth and hard chromate organic film which is extremely thin, colorless and highly adhesive.

The treating liquids to be used in this invention contain proper water soluble resins and hexavalent chrome

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ion and have a pH in the range of from about 5 to about 8. The hexavalent chrome ion acts as an oxidizing agent and at the same time is useful for maintaining proper pH values so that metal surfaces may not be exposed to severe chemical action by said treating liquids.

Another important characteristic of this invention is the use of a dual activator which acts as a moistening agent and an inhibitor into the treating liquid. Since sufficient inactivation is not obtained by just moistening metal surfaces with a treating liquid, in the case of using ordinary treating liquids, repeated applications of coats with a roll coater are required in order to improve inactivation. In the treatment of this invention, however, by virtue of blending a dual activator which combines the two actions of moistening and inhibiting as mentioned in the above, the mere few seconds' contact of metal surfaces to the treating liquids of this invention, without performing repeated coatings by the use of a roll coater, makes it possible to improve remarkably the effect of inactivation. At the same time, the method of this invention has the advantage that the inhibition acts to prevent an excess reaction product from forming on the metal surfaces and also to prevent a reaction product from dissolving into the treating liquid. Thus the formation of an appropriate oxide film on the metal surface and the durability of the treating liquid are extremely improved.

In view of the findings after repeated optical and analytical chemical experiments by the present inventor, it is inferred that in the first step of procedure when the surface is moistened with a treating liquid having a proper pH value and subjected to the action thereof, a proper amount of chromate film, and simultaneously the oxide film of metal in a proper state, are formed on the metal surface during the subsequent heating process carried out at a temperature in the range of from about 110° to about 1000° C. In the second step the combination of said oxide film and resin, or the condensation and polymerization of resins, takes place.

The formation of the oxide film in the heating process is a very important point in the method of this invention. Said formation of the oxide film has an important connection with the pH of the treating liquid and the kind of resins to be used. That is, when the pH is low, a thicker oxide film forms in a large quantity and its composition becomes so coarse on the surface as to be visible to the naked eye. Consequently, the combination thereof with resins is impaired. On the other hand, when the pH is too high, the oxide film forms in less quantity and in a thinner layer, thus reducing the adhesion of an inactivating film, and consequently the desired inactivation cannot fully be attained. It seems that the chemical combining action between the oxide film and the resin layer results in the formation of an inactivating film having strong adhesion, and thus a good inactivating treatment is performed.

Still another feature of this invention is that antioxidation and an electrical inactivating treatment are performed on metal surfaces. This inactivation is useful for protecting metal surfaces from intensive oxidation and for increasing the electrical insulating strength. For example, prior to annealing or curing a thin plate material of beryllium copper alloy, if the treatment of this invention is applied to said material, the formation of

a firm oxide film not easily removed can be prevented and consequently a remarkable effect is obtained in the protection of the metal surface to be applied with coatings. Likewise, if the method of this invention is used in the processing of silicon steel plate, the insulating property thereof can be increased. Moreover, since the treatment of this invention forms a thin layer of 1-8 microns, it is possible to increase and improve the rate of lamination of silicon steel plates.

Still another point, or special feature, of this invention is its suitability for the inactivating treatment of the outer and inner surfaces of a hot spring well and a guide pipe for well water. Although depending somewhat on the kinds of thermal waters, even a stainless steel pipe, not to mention an iron pipe, is corroded by the substances contained in said waters and the pipe diameter becomes smaller, due to the scale thickly adhering therein, thus extremely hampering the drawing and guiding of said waters. However, when the inactivating treatment of this invention is applied to said pipe, corrosion and adhesion of scales is well prevented and a remarkable improvement is given to the handling of hot springs. When a galvanized iron pipe, which is commonly used, was used for drawing water from a well for two months, a scale of about 3 mm. in thickness adhered to the surfaces of the pipe and in the subsequent two years said scale increased to as much as 40 mm. in thickness. Furthermore, during said first two months, corrosion of about 1.5 mm. in depth was produced in a great number of spots. The pipe treated according to this invention showed no change in either the outer or inner surfaces thereof, the gloss of the metal was maintained, and no adhesion of scale was perceived.

The embodiments of this method shall be described in the following:

EXAMPLE 1

Four sheets each of cold beaten steel plate having thicknesses of 1 mm., widths of 90 mm. and lengths of 200 mm., and No. 23 galvanized sheet iron having thicknesses of 0.2 mm., widths of 90 mm. and lengths of 200 mm. were immersed in the inactivating treating liquid set forth below at about 50° C. for 15-60 seconds. Said sheets were taken out of the liquid and heat treated at 170° C. in an atmosphere for 5-10 minutes. Colorless, transparent and hard films were thus formed on said plates.

INACTIVATING TREATING LIQUID (METHOD OF THIS INVENTION)

Water, 1 l., contained with:

Ammonium bichromate	g--	1.76
(As CrO ₃)	g--	1.4
Alkyd melamine resin	g--	80
Moistening agent (Koromin WZ, a cation amine consisting of sodium β -aminopropionate modified by coconut oil, sold by Kao Sekken Kabushiki Kaisha)	g--	3
pH		6.5

For the sake of comparison, eight sheets each of the same two materials as mentioned above were tested by subjecting four sheets of each material to the following two conventional treatments, (a) and (b). The results obtained shall be given later.

Conventional Method (a) (U.S. Patent No. 2,902,390), treating liquid:

Water, 1 l., contained with:

Chromic anhydride	g--	20
25% polyacrylic acid	g--	40
pH		0.9-1.0
Temperature	° C--	50

Said test sheets were immersed in the above treating liquid at 50° C., taken out of said liquid and heated in an electric oven at 150° C. for 5 minutes.

Conventional Method (b) (U.S. Patent No. 2,921,858), treating liquid:

Water, 1 l., contained with:

Vinyl acetate crotonic acid monomer	80 g.
Ammonium bichromate	3 g.
pH	7-9.2 (adjusted with 28% ammonia water).
Temperature	80° C.

Said test sheets were immersed in the above treating liquid at 30° C. for 2-10 seconds, taken out of said liquid and dried in an electric oven at 80° C. for 10 minutes.

Two sheets each of the respective four sheets treated by each of the above-mentioned three different methods were applied with coatings. Untreated sheets (only degreased) and the sheets treated with the aforementioned inactivating treatments but not coated were tested for corrosion resistance. Said coated sheets were put to the test of coating adhesion. The results obtained are shown in the following Tables I and II.

Table I
COLD BEATEN STEEL PLATE

Surface Treatment	Corrosion-resistance test, 5% salt water spray test (JIS-Z-2371)	Coating adhesion test	
		Number of checkered squares (remained unchanged out of 100)	At the part being bent
Untreated	Corrosion produced on the entire surface in 15 minutes.	40/100	Peeling 60%.
Inactivating treatment of this invention.	No corrosion produced in 5 hours. 5-10 spots of red rust appeared in 19 hrs. 10% of red rust produced in 30 hrs.	(Not coated) 100/100 (Coated) 100/100	(Not coated) No change. (Coated) No change.
Conventional Method (a) Treatment.	Several spots of red rust produced in 3 hrs. 10% of red rust produced in 10 hrs.	(Not coated) 100/100 (Coated) 60/100	(Not coated) No change. (Coated). Peeling 10%.
Conventional Method (b) Treatment.	Several spots of red rust produced in 2 hrs. 10% of red rust produced in 7 hrs.	(Not coated) 40/100 (Coated) 80/100	(Not coated) Peeling 10%. (Coated) Peeling 20%.

Table II

JIS NO. 23 GALVANIZED SHEET IRON

Surface Treatment	Corrosion-resistance test, 5% salt water spray test (JIS-Z-2371)	Coating adhesion test	
		Number of checkered squares (remained unchanged out of 100)	At the part being bent
Untreated.....	10% of red rust produced in 75-90 hrs.	80/100.....	Peeling 20%.
Inactivating treatment of this invention.	1-2 spots of white rust pro- duced in 300 hrs.	(Not coated) 100/100....	(Not coated) No change.
	10 some spots of white rust produced in 350 hrs.	(Coated) 100/100.....	(Coated) No change.
Conventional Method (a) Treatment.	10 some spots of red rust produced in 500 hrs.	(Not coated) 100/100....	(Not coated) No change.
	Several spots of white rust produced in 120 hrs.	(Coated) 60/100.....	(Coated) Peeling 10%.
Conventional Method (b) Treatment.	Several spots of red rust produced in 200 hrs.	(Not coated) 90/100....	(Not coated) Peeling 20%.
	10% of red rust produced in 300 hrs.	(Coated) 80/100.....	(Coated) Peeling 10%.

Remarks:

- (1) Coating referred to herein was performed by the use of castor oil denatured aminoalkyd resin (white) applied in two coats, each at 120° C., baked for 80 minutes, the film formed being 30-35 microns in thickness.
- (2) Test of checkered squares: By cut drawing with a recording needle eleven lines lengthwise and breadthwise on the material plate to reach in depth to the under-surface thereof, one hundred checkered squares were made, each side of said squares being 1 mm. A sheet of Scotch paper was pressed against said plate and suddenly peeled off. The checkered squares which did not undergo any change were then counted.
- (3) Bending test: Said test sheet was suddenly bent to an angle of 180° around a mandrel iron rod, the diameter of which is 0.8 mm. After said rod was removed, the bent part of said plate was pressed from both sides. The amount of peeling of the coating at the bent part of said plate was then measured.

EXAMPLE 2

This example is the case of inactivating a guide pipe for hot spring water. Namely, a galvanized iron pipe was immersed in an inactivating treating liquid as set forth below at about 50° C. for 1-2 minutes, taken out of said liquid and heated at 170° C. for 5-10 minutes. A colorless, transparent and hard film was thus produced on said galvanized iron pipe.

INACTIVATING TREATING LIQUID

Water, 1 l., contained with:

Ammonium bichromate.....g--	2.27
(As CrO ₃).....g--	1.8
Alkyd melamine resin modified with coconut oil.....g--	10
Moistening agent (Koromin WZ, a cation amine consisting of sodium β - aminopropionate modified by coconut oil).....g--	3
pH.....	6.0

As described in Example 1, the method of this invention differs from the heretofore known methods of chromate

film or resin film treatments in that it accomplishes a very excellent inactivation by virtue of the synergism among the metal surface, an oxidizing agent, resins and a moistening agent, thus showing a remarkable effect in improving the corrosion-resistance, coating adhesion, antioxidation and electric insulation properties of metal surfaces.

What is claimed is:

1. A method for inactivating metal surfaces which comprises contacting said metal surfaces with an aqueous treating liquid having a pH in the range of from about 5 to about 8, said liquid containing (a) at least one water-soluble thermo-setting resin selected from the group consisting of water-soluble alkyd melamine resins, vegetable oil modified alkyd melamine resins, and polyacrylic acid, (b) a hexavalent chromium compound in an amount such that the CrO₃ content of said liquid ranges up to a maximum of 1.8 grams per liter of said liquid, and (c) a cation amine activating agent consisting of sodium β-amino-propionate modified with coconut oil, and thereafter heating said treated metal surface to a temperature in the range of from about 110° to about 1000° C. to provide an inactivated surface coating on said metal.

2. The method according to claim 1 wherein the amount of said water soluble resin present is in the range of from about 10 to about 80 grams per liter of said liquid.

3. The method according to claim 1 wherein the amount of said hexavalent chromium compound present is such that the CrO₃ content of said liquid is in the range of from about 1.4 to 1.8 grams per liter of said liquid.

4. The method according to claim 1 wherein the amount of said cation amine activating agent present is about 3 grams per liter of said liquid.

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