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ELECTROCHEMICAL TREATMENT OF METAL SURFACES AND THE PRODUCTS THEREOF

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This invention relates to an electrochemical process for forming in a very short time surface coating on iron, steel and aluminum in an aqueous solution consisting essentially of chromic acid and aromatic sulfonic acid containing hydroxyl radical or its water soluble salt to produce an extremely thin coating which increases the corrosion resistance of the metal and the adhesion of paint, varnish, lacquer, and other organic finishes to the metal.

The principal object of this invention is to form in a very short time a thin protective film having a highly corrosion resistant property which is comparable to a conventional thick phosphate or chromate film on the surfaces of base metals such as iron, steel and aluminum. By applying this process, not only a sheet, but also a strip or mechanically formed articles of iron, steel and aluminum can be treated rapidly and economically. Being intrinsically non-porous, the coating produced by applying this process gives iron, steel and aluminum an anti-corrosive property, though the thickness of coating is extremely thin. Even if base metals are exposed at any scratches, cracks or pinholes in the coating, exposed metals may not rust easily because of the self-healing power of the coating.

Another object of this invention is to develop an excellent base for organic coating and improve the adhesion of paint, varnish, lacquer, adhesive, and other organic finishes.

A method of dipping zinc, cadmium and galvanized steel in chromic acid solution containing sulfuric acid or sulfate plus nitric acid to form a chromate coating has been well-known as Unichrome method. This method, however, has not been found successful in treating iron and steel. Another method of dipping aluminum in chromate or dichromate solution containing phosphate and fluoride, or spraying the said solution on aluminum to produce a chromate coating in a short time has been also well-known as Alodine method. Electrochemical methods for coating steel surface in an extremely short time in dichromate solution containing phosphoric acid, or in chromic acid solution containing boric acid, borate or phosphoric acid have been already patented. A process for forming a chromate coating on metals such as steel, aluminum, magnesium, zinc and copper by applying to the surface of the metal a film of an aqueous solution of chromic acid containing a reducing agent and then drying the film on the metal by heating has been developed elsewhere. In spite of these attempts, such a process for forming a highly corrosion resistant coating as described below has not yet been presented.

A distinctive feature of this invention is that the treatment of metals can be performed satisfactorily at low concentration of chemicals used as electrolytes in the treating solution. The most effective concentration of chromic acid in the solution is several percent, and that of aromatic sulfonic acid or sulfonate is in a range of the order of magnitude of 0.01% to 0.1%. Therefore, the cost of chemicals used in this treatment is considerably less than that of those used in a conventional method.

The use of aromatic sulfonic acid or sulfonate containing hydroxyl radical as an addition agent is characteristic of this invention and it is the driving force to make

this treatment successful. The following sulfonic acids or sulfonates are the representative ones used in the solution of this process: catechol-3,5-disulfonic acid or its disodium salt, phenol-2,4-disulfonic acid or its disodium salt, 2-naphthol-3,6-disulfonic acid or its dipotassium salt, 1,8-dihydroxynaphthalene-3,6-disulfonic acid or its disodium salt. These acids or salts are all the aromatic sulfonic acids containing hydroxyl radical or their water soluble salts having a chemical structure which can easily form chelate compounds with metal ions. When a non-porous, anti-corrosive film consisting chiefly of a hydrated oxide of chromium is formed on metal surfaces from an aqueous solution containing hexavalent chromium ion, these sulfonic acids or sulfonates act as a powerful promoter in the film formation and facilitate this formation which has been difficult with other promoters or catalysts even in a considerable amount of addition. Furthermore, they also make it possible to form easily and continuously a light yellow or a light blue colored chromium bearing film having the excellent properties on metal surfaces as described later. We could therefore produce quite freely the various kinds of oxides of chromium which are in different grades of oxidation on the surfaces of cathode metals to be treated in the solution containing chromic acid with the sulfonic acids or sulfonates of this invention. The reason why these sulfonic acids or sulfonates having a chemical structure which can easily form chelating compounds with metal ions are effective in the film formation is still unknown, but from the results of numerous experiments which have been made on a large number of aromatic sulfonic acids or sulfonates, the one having such a structure as mentioned above has been proved advantageous.

The process for forming a suitable coating in this invention depends on concentration of chromic acid, kind and concentration of sulfonic acid or sulfonate, temperature of treating solution, cathodic current density, treating time, and temperature and time of drying after treating. The colors of this coating formed under a variety of these conditions are roughly divided into the following four groups; iridescent yellow, bluish yellow, yellowish blue and almost colorless. According to the gradation of each color of film caused by a little difference of the film formation, dark iridescent yellow, dark yellow, light yellow, light blue and colorless colored film are generally formed. All these films except colorless one have been found to retard corrosion noticeably and metals coated with these films have shown only a few spots of rust after one month outdoor exposure. Especially light yellow and light blue colored films have shown an excellent result. Concerning acid or alkali resistant property, a light blue colored film is best while the dark colored ones have been found to dissolve easily in the solution, although this property depends on a variety of drying conditions. All this can be said about the film coated on iron or steel, and the same may be said about the film on aluminum except that the color of the film becomes colorless under the same condition as that for forming the light colored film on iron or steel. Of these films, the air dried one has an excellent property against the rusting of metals while the film dried by heating under suitable conditions has shown an improved acid, alkali resistant property. The light and almost colorless colored films have been found to be an excellent base for the adhesion of organic coatings and adhesives. The reason why such coatings having plenty of varieties are produced is because of the use of sulfonic acid or sulfonate of this invention. When inorganic or other sulfonic acids are used in the solution for forming chromium bearing film, only dark colored and colorless films are obtained.

The coating weight of produced film is generally from

4 milligrams to 8 milligrams per square decimeter, so the thickness is calculated to be from 0.1 micron to 0.2 micron, assuming that the density of film is 4.

Of the operating conditions, the temperature of treating solution has a remarkable effect on the film formation, and therefore not only the color but also the property of the film produced shows considerable differences with 10° C. changes. In general it is difficult to form a fine, dense coating on metal surfaces below 40° C., so the treating temperature should be above 40° C. At higher temperature a blue rich film is obtained. However, it is not desirable that the temperature exceeds 70° C. because the evaporation loss of water increases rapidly. In this process pure water is preferred, but an increased consumption of pure water by evaporation is not economical. The adhesion of organic finishes is much better on the film produced at higher temperature. The kind of sulfonic acid or sulfonate also plays a very important role in the film formation, so the action of these acids becomes weak for example in the following order: catechol-3,5-disulfonic acid, phenol-2,4-disulfonic acid, 2-naphthol-3,6-disulfonic acid, 1,8-dihydroxynaphthalene-3,6-disulfonic acid. This action of every acid, of course, becomes strong when the acid is used in higher concentration. The influence of concentration of chromic acid on the film formation has also been proved. When other conditions are equal, a dark colored film is obtained in lower concentration of chromic acid, while a light or almost colorless colored film is formed in higher concentration. But a suitable coating can not be obtained from the solution containing more than 100 grams per liter of chromic acid. A corrosion resistant property of the film gradually increases with increasing cathodic current density. At a current density of above from 18 to 20 amperes per square decimeter, however, this property can not be improved appreciably. The adhesion of organic finishes on the film produced at a current density of from about 20 amperes to 22 amperes per square decimeter is superior to that on the film formed at other current densities. To continue the electrolysis for a period of more than 15 seconds has a very good result in forming an excellent corrosion resistant film, but the film produced by the electrolysis for a period of less than 10 seconds has a slightly less corrosion resistant property although it is still comparable to a conventional phosphate or chromate film on corrosion resistance. The period of treating time for forming this chromium bearing film does not affect the adhesion between the filmed metals and organic coatings. Steel plate coated under the most suitable conditions by applying the method of this invention has been proved to show only a very few signs of rust after three months outdoor exposure test.

When iron or steel is treated initially as anode, then as cathode in the solution of this invention, or by changing the polarity periodically during the treatment, the light colored film usually formed under normal conditions changes to dark.

Considering these points, I present the range of the most suitable operating conditions as below.

Chromic acid (CrO_3)_____g./l__	20~100
Aromatic sulfonic acids containing hydroxyl radical, or their water soluble salts specified in this invention__g./l__	0.2~4.0
Treating temperature_____° C__	40~70
Cathodic current density____a./sq. dm__	More than 15
Treating time_____sec__	1~30

A suitable amount of each sulfonic acid or sulfonate in each case is given later in the examples of procedure.

Furthermore, all the films formed by my method have various colors as described above, but they are transparent, so if metals to be treated finish brightly, the treated surfaces of metals remain bright and show a very beautiful appearance in comparison with that of thick phosphated surfaces. There is an advantageous fact that the original colors of the film formed on metal surfaces can not be seen though the coated organic films on them when clear organic coatings are applied on the filmed metal surfaces.

Having an extremely strong bond to base metal, the film formed by my method does not peel off at all in any mechanical forming operations usually applied. However, if it is subjected to such a severe forming operation as deep drawing, it may be damaged and subsequently base metal can be exposed and finally rusted. In such a case an organic coating or a rust preventive oil is needed to protect the area mechanically formed. Hardness, scratch resistance, impact resistance and other physical and mechanical properties of the film made according to my process are similar to those of a bluing film which is a blue thin iron oxide.

The following are some examples of effective coating operations.

Example 1

Commercial cold rolled low carbon steel (black plate) 0.25 millimeter thick is cleaned with trichloroethylene vapor and electrolytically cleaned in alkaline solution, washed with water, pickled in hydrochloric acid, washed again with water, then cathodically treated according to the following (lead electrode is used as anode):

Chromic acid_____g./l__	20
Disodium phenol-2,4-disulfonate_____g./l__	0.3~1.4
Treating temperature_____° C__	50
Cathodic current density_____a./sq. dm.__	20
Treating time_____sec__	20

The film obtained has iridescent yellow color after air drying and the treated steel shows few spots of rust after about one month outdoor exposure.

Example 2

The same steel plate as the one used in Example 1 is treated cathodically under the following conditions.

Chromic acid_____g./l__	50
Catechol-3,5-disulfonic acid_____g./l__	0.2~1.0
Treating temperature_____° C__	60
Cathodic current density_____a./sq. dm__	18
Treating time_____sec__	20

The film obtained has light blue color after air drying. The treated steel shows no sign of rust after one month outdoor exposure, and also proves no appearance of red rust after 240 hours' salt spray test (JIS–Z2371). Under this salt spray test, a conventional phosphate coated steel rusts entirely within several hours.

Example 3

The same steel plate as the one used in Example 1 is treated cathodically as follows:

Chromic acid_____g./l__	100
Disodium-2-naphthol-3,6-disulfonate ____g./l__	0.5~2.0
Treating temperature_____° C__	50
Cathodic current density_____a./sq. dm__	22
Treating time_____sec__	20

The film obtained has light blue color after air drying and the results of corrosion test on the treated steel are same as those on one obtained by the procedure of Example 2.

Two 50 millimeters length and 50 millimeters width sheets are cut from the treated sample, then they are bonded together by using epoxy adhesive, the bonding strength obtained being 3.5 kilograms per centimeter as the result of peel off test. In the case of a conventional phosphate coated steel, the bonding strength, however, is usually within a range of from 1.0 kilogram to 2.0 kilograms per centimeter.

Example 4

Commercial cold rolled medium carbon steel 0.25 millimeter thick is subjected to the same pretreatment as described in Example 1, then cathodically treated according to the following:

Chromic acid	g./l.	70
Disodium-1,8-dihydroxynaphthalene-3,6-disulfonate	g./l.	1.0~4.0
Treating temperature	° C.	70
Cathodic current density	a./sq. dm.	20
Treating time	sec.	20

The film obtained has light yellowish blue color after air drying and the treated steel rusts slightly after one month outdoor exposure.

Example 5

Commercial 99.0% aluminum sheet 0.7 millimeter thick is cleaned in alkaline solution, washed with water, then subjected to cathodic treatment under the following conditions.

Chromic acid	g./l.	50
Disodium phenol-2,4-disulfonate	g./l.	0.3~1.4
Treating temperature	° C.	50
Cathodic current density	a./sq. dm.	20
Treating time	sec.	20

The film obtained has no color and non-porous, because hardly any copper deposition can be observed on the entire surface of the film after one hour immersion test in copper sulfate solution (pH 2.8) at room temperature.

The products of the method described are resistant to corrosion even when tested under atmospheric condition, and this resistance is greatly increased by a very thin organic coating such as that oridinarily applied to tinplate to be used as can stock. The products can therefore be used under such a severe condition as untreated metals have never been adapted. The adherence of organic coating is also materially improved by the treatment. Flaking and peeling of the organic coating do not occur on normal drawing or forming of the treated metals. When coated by suitable organic films, the products are thus adapted for use as substitutes for tinplate, terneplate, galvanized steel or anodized aluminum.

What is claimed is:

1. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having a metal surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of an aromatic disulfonic acid containing a phenolic hydroxyl group and being adapted to form a chelate compound with a metal ion.

2. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having a metal surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of a water soluble salt of an aromatic disulfonic acid containing a phenolic hydroxyl group and being adapted to form a chelate compound with a metal ion.

3. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having a metal surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of an aromatic disulfonic acid containing a phenolic hydroxyl group and being adapted to form a chelate compound with a metal ion and being selected from the group consisting of catechol-3,5-disulfonic acid, phenol-2,4-disulfonic acid, 2-naphthol-3,6-disulfonic acid, 1,8-dihydroxynaphthaline-3,6-disulfonic acid, and water soluble salts thereof.

4. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having an iron surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of an aromatic disulfonic acid containing a phenolic hydroxyl group and being adapted to form a chelate compound with a metal iron.

5. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having an iron surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of a water soluble salt of an aromatic disulfonic acid containing a phenolic hydroxyl group and being adapted to form a chelate compound with a metal ion.

6. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having an aluminum surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of an aromatic disulfonic acid containing a phenolic hydroxyl group and being adapted to form a chelate compound with a metal ion.

7. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having an aluminum surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of a water soluble salt of an aromatic disulfonic acid containing a phenolic hydroxyl group and being adapted to form a chelate compound with a metal ion.

8. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having a metal surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of catechol-3,5-disulfonic acid.

9. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having a metal surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of the disodium salt of catechol-3,5-disulfonic acid.

10. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having a metal surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of phenol-2,4-disulfonic acid.

11. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having a metal surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of the disodium salt of phenol-2,4-disulfonic acid.

12. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having a metal surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of 2-naphthol-3,6-disulfonic acid.

13. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having a metal surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of the dipotassium salt of 2-naphthol-3,6-disulfonic acid.

14. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having a metal surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of 1,8-dihydroxynaphthalene-3,6-disulfonic acid.

15. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having a metal surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per

liter of chromic acid, and 0.2–4.0 grams per liter of the disodium salt of 1,8-dihydroxynaphthalene-3,6-disulfonic acid.

16. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having a metal surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of an aromatic disulfonic acid containing a phenolic hydroxyl group and being adapted to form a chelate compound with a metal ion at a current density of more than 15 amperes per square decimeter.

17. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having a metal surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of a water soluble salt of an aromatic disulfonic acid containing a phenolic hydroxyl group and being adapted to form a chelate compound with a metal ion at a current density of more than 15 amperes per square decimeter.

18. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having a metal surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of an aromatic disulfonic acid containing a phenolic hydroxyl group and being adapted to form a chelate compound with a metal ion at a temperature of 40–70° C.

19. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having a metal surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of a water soluble salt of an aromatic disulfonic acid containing a phenolic hydroxyl group and being adapted to form a chelate compound with a metal ion at a temperature of 40–70° C.

20. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having a metal surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of an aromatic disulfonic acid containing a phenolic hydroxyl group and being adapted to form a chelate compound with a metal ion for 1–30 seconds.

21. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having a metal surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of a water soluble salt of an aromatic disulfonic acid containing a phenolic hydroxyl group and being adapted to form a chelate compound with a metal ion for 1–30 seconds.

22. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having a metal surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of an aromatic disulfonic acid containing a phenolic hydroxyl group and being adapted to form a chelate compound with a metal ion at a current density of more than 15 amperes per square decimeter for a period of 1–30 seconds at a temperature of about 40–70° C.

23. A method of forming a protective coating on a metal surface, which comprises subjecting as cathode an article having a metal surface to electrolysis in an aqueous solution consisting essentially of water, 20–100 grams per liter of chromic acid, and 0.2–4.0 grams per liter of a water soluble salt of an aromatic disulfonic acid containing a phenolic hydroxyl group and being adapted to form a chelate compound with a metal ion at a current density of more than 15 amperes per square decimeter for a period of 1–30 seconds at a temperature of about 40–70° C.

24. An article having a metal surface protected by a thin, non-porous, corrosion-resistant coating consisting essentially of a film composed of a chelate of said metal and a reduced aromatic disulfonic acid initially containing a phenolic hydroxyl group and of reduced chromic acid in the form of hydrated chromium oxide.

25. An article having an iron surface protected by a thin, non-porous, corrosion-resistant coating consisting essentially of a film composed of a chelate of said iron and a reduced aromatic disulfonic acid initially containing a phenolic hydroxyl group and of reduced chromic acid in the form of hydrated chromium oxide.

26. An article having an aluminum surface protected by a thin, non-porous, corrosion-resistant coating consisting essentially of a film composed of a chelate of said aluminum and a reduced aromatic disulfonic acid initially containing a phenolic hydroxyl group and of reduced chromic acid in the form of hydrated chromium oxide.

27. An article having a metal surface protected by a thin, non-porous, corrosion-resistant coating of a thickness of about 0.1–0.2 micron consisting essentially of a film composed of a chelate of said metal and a reduced aromatic disulfonic acid initially containing a phenolic hydroxyl group and of reduced chromic acid in the form of hydrated chromium oxide.

28. A coated article produced by the method of claim 1.

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