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PROCESS FOR PRODUCING DYED CHROMATE FILMS ON ZINC AND ZINC ALLOYS

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10 Claims. (Cl. 148—6.1)

ABSTRACT OF THE DISCLOSURE

Chromate films which can be dyed with organic dyes are obtained by treating zinc or zinc alloys with a solution consisting essentially of chromic acid, an inorganic chloride and an inorganic sulfate.

This invention relates to processes for chromate-treating zinc and zinc alloys.

Many chromate-treating processes have been recently studied but no treating process which can bring about a high corrosion resistance and a fine appearance has yet been suggested. In order that zinc may be used for ornamentation, it must be high in corrosion resistance and having a pleasing appearance. However, as the chromate film is thin, such as a fraction of one micron thick, it does not have a corrosion resistance as high as that of anodized aluminum, is poor in luster and is apt to produce blots.

The conventionally used chromate bath is generally made by adding a small amount of a strong acid, such as hydrochloric acid, such nitric acid or sulfuric acid to chromic acid or chromate so that passive films may be removed and the production of chromate films may be accelerated. However, as a free acid is used, zinc will be dissolved so much as to produce surface blots and become lusterless. Further, if a chloride in an amount of more than 2 g./l. is added to a chromate bath, the surface coarseness will increase. Therefore, such addition has been considered unfavorable and the use of the chloride has been avoided. The chromate film is so porous as to be able to be dyed by absorbing an organic dye. But, if the chromate film is not high in adhesion, when it is dyed, it will be apt to peel off. Therefore, the corrosion resistance of a dyed chromate film generally tends to be lower than that of a chromate film not dyed. For example, even when a chromate film has such high corrosion resistance as 200 hours in a salt spray test, if it is dyed, the corrosion resistance will remarkably reduce. Thus, the conventional product has a defect that the corrosion resistance and dyeability are not compatible therein.

An object of the present invention is to eliminate such defects as are mentioned above and to provide a treating process for forming uniform chromate films which are high in luster, adhesion and dyeability and which will not become lower in corrosion resistance when dyed. The subject matter of the present invention is characterized by treating zinc or zinc alloys with a chromic acid solution in which proper amounts of an inorganic chloride and an inorganic sulfate are dissolved.

For the inorganic chloride that can be used in the present invention there can be enumerated, for example, not only such alkali metal cholrides as sodium chloride, such chlorides of alkaline earth metals as magnesium chloride and calcium chloride and most of such metal chlorides as cobalt chloride, copper chloride, zinc chloride

and nickel chloride but also ammonium chloride which is not a metal chloride but which has the same performance and effect as the chlorides tested above. Specially sodium chloride and ammonium chloride are so low in cost and so economical that they are recommended for carrying out the present invention.

For the inorganic sulfate there can be used such alkali metal sulfates as sodium sulfate, such sulfates of alkaline earth metals as calcium sulfate and magnesium sulfate and many of the metal sulfates as zinc sulfate, copper sulfate, such nickel sulfate, chromium sulfate and titanium sulfate.

In practice, a solution containing chromic acid as a main agent and 10 to 50 g./l. of each of the chloride and sulfate mentioned above and, if required, a proper amount of zinc oxide, may be used to make a chromate bath and a metal plate made of zinc or a zinc alloy may be immersed in said solution and may be treated at a bath temperature of 15 to 60° C. for 5 to 120 seconds. In such case, the purpose of using zinc oxide is to serve to adjust the treating time by regulating the pH as a neutralizing agent. The metal plate treated by such process will show an excellent luster due to the simultaneous actions of erosion by chlorine ions and chemical polishing by the metal sulfate and a chromate film high in adhesion will be formed. Even when the metal plate is dyed for ornamentation, the corrosion resistance of the chromate film will not be lowered at all.

An example of the luster value of the chromate film obtained by the process of the present invention is shown in the following table as compared with those of conventional products.

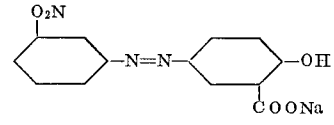
Test samples:	Luster degrees (rates of reflection on a mirror surface at 60 degrees)
Chromate film by the process of the present invention	342
Chromate film by the known process	167
Commercial pre-coated galvanized steel sheet	80
Golden dyed anodized aluminum sheet	190

That is to say, the luster degree of the film made by the process of the present invention is more than twice as high as of the chromate film formed by adding such strong acid as sulfuric acid, nitric acid or hydrochloric acid in the known process.

Typical examples of the present invention shall be described in the following:

Example 1

A chromate bath composed of 100 g./l. of chromic acid, 10 g./l. of ammonium chloride and 30 g./l. of zinc sulfate was prepared. When a zinc plate was immersed in this solution and was treated at a bath temperature of 30° C. for 10 seconds, a uniform lustrous chromate film high in adhesion was formed on the surface of the zinc plate. When the zinc plate on which the chromate film was thus produced was washed with water and was then immersed in a dyeing solution containing 2 g./l. of such yellow alizarin dye as, for example, an alizarin yellow dye having a structural formula of 3-nitroaniline azo coupled to sodium salicylate



at 60° C. for 10 minutes, it was dyed yellow. When this dyed plate was washed with water and was dried, there was obtained a fine yellow zinc plate capable of long practical use.

In such salt spray test as, for example, under the following conditions:

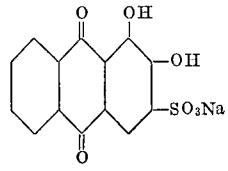
Salt water	5%.
Temperature	35° C.
Spray pressure through the nozzle	15 kg./cm.². Inclined by 30 degrees
Position of the sample	to the vertical.
Spraying time	100 hours.

no white corrosion product was produced at all, the dye did not fade away and an excellent corrosion resistance was shown.

Example 2

A die-cast product made of a zinc alloy containing 4% aluminum, 3% copper and 0.05% magnesium was immersed in a chromate solution composed of 80 g./l. of chromic acid, 10 g./l. of sodium chloride and 30 g./l. copper sulfate and was treated at 40° C. for 3 seconds.

When the zinc die-cast product on which a chromate film was thereby produced was washed with water and was then immersed in a dyeing solution containing 2 g./l. of such red alizarin dye as, for example, an alizarin red dye having a structural formula of sodium 1,2-dihydroxy anthraquinone-3-sulfonate

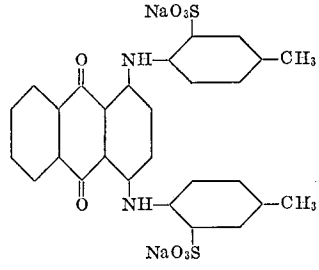


at 60° C. for 3 minutes, it was dyed red. When this dyed product was washed with water and was then dried, a fine red die-cast product high in corrosion resistance was obtained.

Example 3

A so-called zinc alloy plate containing 0.4 to 3.0° copper, 0.05 to 0.16% titanium and 0.02 to 0.03% chromium was immersed in a chromate solution composed of 80 g./l. of chromic acid, 20 g./l. of ammonium chloride and 30 g./l. of zinc sulfate and was treated at room temperature for 20 seconds.

When the zinc alloy plate on which a chromate film was thereby produced was washed with water and was then immersed in a dyeing solution containing 2 g./l. of such green alizarin dye as, for example, an alizarin green dye having a structural formula of sodium 1,4-di-ortho-sulfo-para-tolyl amino anthraquinone



for 5 minutes, it was dyed green. When this dyed plate was washed with water and was dried, a fine green zinc alloy plate high in corrosion resistance was obtained.

Example 4

A chromate bath composed of 100 g./l. of chromic acid, 10 g./l. of cobalt chloride and 30 g./l. of zinc sulfate was prepared. When a zinc plate was immersed in this solution and was treated in the same manner as in Example 1, a uniform lustrous chromate film high

in adhesion was formed on the surface of the zinc plate. The dyeability and anticorrosiveness with the dye of this zinc plate showed the same results as in Example 1.

Example 5

A chromate bath composed of 100 g./l. of chromic acid, 10 g./l. of copper chloride and 30 g./l. of copper sulfate was prepared. When a zinc plate was immersed in this solution and was treated in the same manner as in Example 1, it showed the same results.

Example 6

When a zinc plate was immersed and treated in the same manner as in Example 1 in a chromate bath composed of 100 g./l. of chromic acid, 10 g./l. of magnesium chloride and 30 g./l. of zinc sulfate, the same results were obtained.

Example 7

A chromate bath composed of 100 g./l. of chromic acid, 10 g./l. of sodium chloride and 30 g./l. of sodium sulfate was prepared. When a zinc plate was immersed in this solution and was treated in the same manner as in Example 1, a lustrous chromate film excellent in adhesion was formed on the surface of the zinc plate. The dyeability of this zinc plate showed the same favorable results as in Example 1.

Example 8

When a zinc plate was immersed and treated under the same conditions as in Example 1 in a chromate bath composed of 100 g./l. of chromic acid, 10 g./l. of ammonium chloride and 30 g./l. of magnesium sulfate, a uniform lustrous chromate film was formed on the surface of the zinc plate. The corrosion resistance of this zinc plate when dyed in the same manner as in Example 1 showed excellent results.

What is claimed is:

1. A process for producing dyed chromate films on zinc and zinc alloys, which comprises treating a zinc or a zinc alloy article with a solution, the dissolved constituents of which consist of chromic acid, an inorganic chloride salt and an inorganic sulfate salt; said chromic acid comprising the sole source of hydrogen ions in the solution; washing the article after the treating step; and then dyeing the article.

2. A process for producing dyed chromate films on zinc and zinc alloys according to claim 1 wherein said inorganic chloride salt is an alkali metal chloride.

3. A process for producing dyed chromate films on zinc and zinc alloys according to claim 1 wherein said inorganic chloride salt is a chloride of an alkaline earth metal.

4. A process for producing dyed chromate films on zinc and zinc alloys according to claim 1 wherein said inorganic chloride salt is a metal chloride selected from a group consisting of cobalt chloride, copper chloride, zinc chloride and nickel chloride.

5. A process for producing dyed chromate films on zinc and zinc alloys according to claim 1 wherein said inorganic chloride salt is ammonium chloride.

6. A process for producing dyed chromate films on zinc and zinc alloys according to claim 1 wherein said inorganic sulfate salt is an alkali metal sulfate.

7. A process for producing dyed chromate films on zinc and zinc alloys according to claim 1 wherein said inorganic sulfate salt is a sulfate of an alkaline earth metal.

8. A process for producing dyed chromate films on zinc and zinc alloys according to claim 1 wherein said inorganic sulfate salt is a metal sulfate selected from a group consisting of zinc sulfate, copper sulfate, nickel sulfate, chromium sulfate and titanium sulfate.

9. A process according to claim 1, in which the inorganic chloride salt and the inorganic sulfate salt are each present in the solution in an amount of from 10 to 50 g./l.

10. A process according to claim 1, in which the article is immersed in said solution for from 5 to 120 seconds and the solution has a temperature of 15 and 60° C.

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