United States Patent

[11] 3,615,897

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[21] Appl. No. **808,687**
[22] Filed **Mar. 19, 1969**
[45] Patented **Oct. 26, 1971**
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[54] **BLACK FILMS FOR METAL SURFACES**
7 Claims, No Drawings

[52] **U.S. Cl.** **148/6.24,** 148/6.15, 148/6.16
[51] **Int. Cl.** **B44d 5/00**
[50] **Field of Search** 148/6.14, 6.15, 6.16, 6.24

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ABSTRACT: A black, smutlike film, resistant to rub off, and uniform in appearance and thickness, is deposited on a metal surface by contacting the surface with an aqueous acidic solution containing bismuth, hydrogen, nitrate, and sulfate ions. The blackened surface is rendered corrosion resistant by further treatment with a phosphating solution to deposit a phosphate conversion coating thereon.

BLACK FILMS FOR METAL SURFACES

The present invention concerns coatings for metal surfaces. More particularly, the present invention concerns an improved method for producing corrosion-resistant blackened ferrous metal surfaces. Even more particularly, the present invention relates to an improved bath for depositing a strongly adherent, black film on ferrous metal surfaces.

The use of blackened, corrosion-resistant ferrous metal surfaces for imparting decorative appearances to a variety of assemblies and parts has found wide application in the automotive industry. The prior art is replete with compositions and techniques adapted to provide these blackened, corrosion-resistant surfaces. Initially, the art reveals methods wherein a phosphated metal surface is subsequently coated with either a black paint, stain, ink, or dye which is introduced onto the surface either in an aqueous medium or as a sealant in a rust-preventive oil. These methods of coloring enjoy only moderate success because of the nonuniformity, susceptibility to fading, and nonpermanence occasioned with their use.

Today, one of the common methods for providing blackened, corrosion resistant surfaces comprises a two-step procedure of (1) blackening the surface and then (2) applying a protective coating to the blackened surface. The blackening step is usually carried out by immersing the metallic surface or substrate in an aqueous acidic solution having nitrate and either bismuth or antimony ions contained therein. The black, smutlike film deposited thereby is then fixed to the surface by treatment with a zinc phosphate solution which simultaneously renders the substrate corrosion resistant. Although the films in and of themselves do not afford adequate corrosion resistance, bismuth films have been found to provide nearly twice the corrosion resistance of antimony. And while it is the subsequent phosphating of the surface that imparts the bulk of the corrosion resistance to the surfaces, it would be desirable to take advantage of the increased corrosion resistance imparted by the bismuth film.

Although both bismuth films and antimony films are subject to removal by manual rubbing bismuth films, disadvantageously, are susceptible to rub off even under running tap water exerting a pressure of less than 1 p.s.i.g. However, because bismuth films afford nearly twice the corrosion resistance of antimony films- a solution to the problem of rub off would provide an important advance in the art.

Accordingly, it is an object of the present invention to provide an improved bismuth black film for ferrous metal surfaces which is resistant to rub off upon subjection to a running water tap and which presents a uniform thickness and appearance. A further object of the present invention is to provide an improved method for producing bismuth-blackened corrosion-resistant metal surfaces. It will become apparent to those skilled in the art that these and other objects are achieved by the present invention on reference to the following detailed description.

In accordance with the present invention, a ferrous metal surface, such as iron, steel alloys and the like, is rendered corrosion resistant by first contacting the surface with an aqueous acidic solution containing bismuth, nitrate, hydrogen and sulfate ions to deposit a black, smutlike film thereon. Although it is feasible to utilize the present invention with other metals which can receive a phosphate coating, the present invention is particularly applicable to ferrous metals. Thereafter, the blackened surface is contacted with a phosphate solution to deposit a phosphate conversion protective coating thereon. Optionally, the phosphate coating may then be passivated by treatment with chromic acid, or chromic-phosphoric acid. The coating is then usually sealed with a rust-preventive oil, wax, water-emulsifiable oil or the like.

In one embodiment, the present invention contemplates a novel bath for depositing black films on metal surfaces. It has now unexpectedly been discovered that by incorporating concentrations of sulfate ion into an aqueous acidic bismuth and nitrate ion containing solution, a black film which has improved resistance to rub off is imparted to metal surfaces contacted therewith. This discovery has obviated the drawbacks to the use of bismuth films that were heretofore encountered.

The sulfate ion utilized in the present bath can be introduced into solution in any convenient manner, such as by a sulfate salt or an acid. It is also within the purview of the invention to add to the acidic solution suitable sulfate ion producing reagents, such as the complex of dimethyl thiourea and nitric acid. However, because of economic consideration, it is preferred to employ the sulfate salts or acid. As noted, any sulfate salt is suitable for use in preparing the film-forming solutions of the invention. Examples of such salts include bismuth sulfate, calcium sulfate, sodium sulfate, potassium sulfate, and the like. However, because of its availability and low cost, sulfuric acid is the most practical sulfate ion source to use. Additionally, sulfuric acid is an excellent source of free hydrogen ions in the present solutions.

The effective concentration of the sulfate ion in the acidic solution has been found to be variable over a wide range. Concentrations ranging from about 0.15 to 8.0 percent of sulfate based on the weight of the solution are effective. Preferably from about 1.0 to 5.0 percent by weight of the solution is comprised of the sulfate ion.

The bismuth ion can be present in the bath either as a salt or as the anhydrous powder metal. Any bismuth salt can be employed, such as, bismuth chloride, bismuth sulfate, bismuth nitrate, bismuth oxide, and the like. Preferably, the bismuth ion is introduced into the acidic solution as an anhydrous metal powder. Concentrations ranging from 0.01 to 1.0 weight percent of the ion in an acid solution having from 0.01 to 0.2 weight percent of hydrogen ion are preferred. Concentrations of the hydrogen ion greater than 0.2 weight percent promote pickling and are to be avoided.

In formulating the baths within the above-defined percentages, it is necessary to maintain certain weight ratios of the ions. These ratios may be summarized as follows:

1. There must be a minimum sulfate ion to bismuth ion weight ratio of from 7.7:1 to 15.4:1, and usually at least about 10:1. If the weight ratio falls below the understood minimum, then the adhesion of the bismuth film to the metal substrate is quite poor. The maximum weight ratio of sulfate ion to bismuth ion is limited only by economic considerations. Generally, however, from about a 20:1 to 50:1 weight ratio can be used, preferably from about 30:1 to 40:1.
2. The weight ratio of hydrogen ion to bismuth ion is critical, for otherwise the bismuth ion does not go into solution or is incompletely solubilized. It has been found that the hydrogen ion to bismuth ion weight ratio must be at least 1:13 and cannot exceed about 1:1.3 since at higher ratios the metal substrate is subject to pickling.
3. The nitrate radical which is introduced into the solution as nitric acid is present in a weight ratio of 1.5:1 to 2.5:1 times that of the bismuth concentration, preferably about 2.0:1. Hence, the nitrate radical comprises from about 0.15 to 2.5 percent by weight of the solution and preferably from 0.2 to 2 percent by weight of the solution. The balance of the solution comprises water.

Optionally, a stannous ion, comprising about 0.001 to 1.0 percent by weight of the solution, may be incorporated into the bath. The stannous ion accelerates and enhances deposition of the bismuth film on the metal surface. Preferably, the stannous ion can be provided by a stannous salt, such as stannous chloride which ionizes in acidic solutions.

When a metal surface is contacted, preferably by immersion, with this novel bath for a period of about 0.25 to 10 minutes and at a temperature of about 20° to 35° C., a black, smutlike film, resistant to rub off under a running water tap exerting pressures of greater than 35 p.s.i.g. and of uniform thickness and appearance, is deposited on the metal surface.

After the smutlike film is deposited on the metal surface a protective coating is thereafter applied. Any one of a variety of well-known coatings can be used. It is preferred, however, to apply a phosphate coating to the blackened surface. The

phosphate coatings vary widely in composition and they generally comprise aqueous acidic solutions containing phosphate, zinc, nitrate, and ferrous ions. It is, usually, advantageous to have at least one ion selected from the group of calcium, nitrate, chlorate, lithium, cobalt, and nickel ions present as an auxiliary ion. Any such conventional solution having phosphate, zinc, nitrate and ferrous ions and in which there is, preferably, incorporated nickel ions is contemplated by the present invention. These solutions are commercially available and are satisfactory for use in practicing the present invention.

The phosphate coatings are generally applied by an immersion technique. The conventional procedure generally associated with their application comprises contacting the blackened surface with about a 3 to 4 percent by weight aqueous acidic zinc phosphate solution at about 60° to 95° C. for about 5 to 30 minutes and thereafter rinsing and drying the surface by conventional techniques. The phosphate coating that is deposited fixes the black film to the surface and simultaneously renders the surface corrosion resistant.

Optionally, the zinc phosphate coating can be passivated. This entails the application of a coating of either a chromic acid or a chromic-phosphoric acid (modified chromic acid) solution to the phosphated surface. Such chromating solutions are widely known and commercially available, usually, in concentrated solutions. Dilute aqueous solutions of these concentrated chromating solutions ranging from 6 to 16 ounces of concentrate per 100 gallons (gal.) of solution; preferably 8 to 12 ounces of concentrate per 100 gal. of solution are conventionally utilized to passivate the conversion coating.

Usually, an immersion technique is employed to passivate the phosphate coating although spray techniques can be utilized for light metal objects. Generally, the blackened, phosphated surface is immersed in an aqueous bath, such as described above, for a period of from 15 to 60 seconds, desirably about 30 seconds at elevated temperatures of about 70° to 90° C., preferably at about 75° C.

If the surface is passivated it may either be rinsed and dried or may have a sealant directly applied to it. If the surface is not passivated, then a sealant is directly applied. In any event, the final step in the process comprises the sealing of the blackened, phosphated surface.

As in known in the art any suitable organic oil, wax water-emulsifiable oil or the like will suffice as a sealant for the phosphate coating.

Again, in applying the sealant, an immersion technique is generally employed. The surface is immersed in an aqueous solution usually having from about 5 to 30 percent by volume of the sealant contained therein for a period of about 1 to 10 minutes and at elevated temperatures of about 70° to 90° C. The high temperature promotes drainage and dry-off of any excess sealant on the surface.

The following examples, which are not to be construed as unduly limitative of the present invention, set forth specific embodiments of the present invention which exhibit the heretofore defined qualities and properties. Unless otherwise indicated all percentages are by weight.

EXAMPLE I

A 2 inch ×4 inch 1010 carbon steel panel was immersed at about 24° C. in a black film bath which has the following composition:

	Wt. % of Solution
Bi^{+3} (introduced as anhydrous metal powder)	0.65
$SO_4^{=}$ (introduced as H_2SO_4)	7.98
NO_3^{-1} (introduced as HNO_3)	1.30
H^+ (introduced as HNO_3 and H_2SO_4)	0.20
H_2O	89.87
	100.00%

After about 0.25 minutes the surface was completely and uniformly blackened. The panel was then subjected to a running water tap exerting a pressure of at least 35 p.s.i.g. The black film remained deposited on the metal substrate with no evidence of rub off.

EXAMPLE II

A 2 inch ×4 inch 1010 carbon steel panel was immersed at 24° C. in a black film bath having the following composition:

	Wt. % of Solution
Bi^{+3} (introduced as anhydrous metal powder)	0.13
$SO_4^{=}$ (introduced as H_2SO_4)	3.99
NO_3^{-1} (introduced as HNO_3)	0.26
H^+ (introduced as HNO_3 and H_2SO_4)	0.10
H_2O	95.42
	100.00%

After 3 minutes a black film was deposited in the panel. The film did not rub off under a water pressure of 35 p.s.i.g.

EXAMPLE III

The procedure of example I was followed except that the bath had the following composition:

	Wt. % of Solution
Bi^{+3} (introduced as anhydrous metal powder)	0.065
$SO_4^{=}$ (introduced as H_2SO_4)	2.000
NO_3^{-1} (introduced as HNO_3)	0.130
H^+ (introduced as H_2SO_4 and HNO_3)	0.050
H_2O	97.755
	100.000%

The black film was deposited in 4 minutes. Comparable results were obtained when the blackened surface was subjected to a running water tap exerting a pressure of 35 p.s.i.g.

EXAMPLE IV

Again, the procedure of example I was followed except that the bath had the following composition:

	Wt. % of Solution
Bi^{+3} (introduced as anhydrous metal powder)	0.0325
$SO_4^{=}$ (introduced as H_2SO_4)	1.0000
NO_3^{-1} (introduced as HNO_3)	0.0650
H^+ (introduced as H_2SO_4 and HNO_3)	0.0250
H_2O	98.8775
	100.0000%

Testing for rub off under the same conditions as in example I gave comparable results.

EXAMPLE V

The procedure of example I was followed except that the black film bath had the following composition:

	Wt. % of Solution
Bi^{+3} (introduced as anhydrous metal powder)	0.01625
$SO_4^{=}$ (introduced as H_2SO_4)	0.50000
NO_3^{-1} (introduced as HNO_3)	0.03250
H^+ (introduced as H_2SO_4 and HNO_3)	0.01250
H_2O	99.43875
	100.00000%

Testing for rub off under the same conditions as in example I gave comparable results.

EXAMPLE VI

1 gallon samples of the bath of example II were tested for surface area coverage, i.e., the amount of surface area that could effectively have deposited thereon a black film of the type herein described.

It was found that 32 square feet of 1010 carbon steel could effectively be coated with a black film by immersing the steel panels in the bath for 7 minutes. It was also found that 24 square feet of steel panels could effectively be coated if immersion time in the solution was 5 minutes.

EXAMPLE VII

To illustrate the improved adherence of the present films, a 2 inch×4 inch 1010 carbon steel panel was immersed at 24° C. in a black film bath having the following composition:

	Wt. % of Solution
Bi^{+3} + (introduced as anhydrous metal powder	0.130
NO_3^{-1} (introduced as HNO_3)	9.600
H^+ (introduced as HNO_3)	0.095
H_2O	90.175
	100.000%

After 3.5 minutes a black film was deposited on the panel.

When the blackened panel was subjected to a running water tap pressure of 1 p.s.i.g., the black film washed off. Hence without the presence of the sulfate ion in the bath, the deposited black films are readily susceptible to rub off under running water tap pressures well below those of the films deposited from sulfate ion containing baths.

What is claimed is:

1. A bath for depositing a black film on a ferrous metal surface consisting essentially of:
   a. from about 0.01 to 1.0 percent by weight of bismuth ions;
   b. from about 0.015 to 2.5 percent by weight of nitrate ions;
   c. from about 0.01 to 0.20 percent weight of hydrogen ions;
   d. from about 0.25 to 8.0 percent by weight of sulfate ions;
   e. from about 99.715 to 89.30 percent by weight of water; and wherein the minimum sulfate ion to bismuth ion weight ratio is from 7.7:1 to 15.4:1.

2. The bath of claim 1 wherein:
   a. said bismuth ion is present in a weight ratio to said hydrogen ion of from 13:1 to 3.25:1;
   b. said sulfate ion is present in a weight ratio to said bismuth ion of at least 10:1; and
   c. said nitrate ion is present in a weight ratio to said bismuth ion of from 1.5:1 to 2.5:1.

3. The bath of claim 1 and further including from about 0.001 to 1.0 percent by weight of a stannous ion.

4. A method for producing a blackened, corrosion-resistant ferrous metal surface comprising:
   a. contacting said surface at about 20° to 30° C. for about 0.25 to 10 minutes with an aqueous acidic bath comprising:
      1. from about 0.01 to 1.0 percent by weight of a bismuth ion;
      2. from about 0.015 to 2.50 percent by weight of a nitrate ion;
      3. from about 0.01 to 0.20 percent by weight of a hydrogen ion;
      4. from about 0.25 to 8.00 percent by weight of a sulfate ion;
      5. from about 99.715 to 89.30 percent by weight of water; and wherein the minimum sulfate ion to bismuth ion weight ratio is from 7.7:1 to 15.4:1, thereby depositing a black film on said surface;
   b. thereafter contacting said blackened surface with a zinc phosphating solution, thereby depositing a phosphate conversion coating thereon; and
   c. sealing said coated surface by contacting said surface with a sealant.

5. The method of claim 4 wherein prior to said sealant being applied, said surface is passivated by contacting said surface with an aqueous acidic solution selected from the group consisting of chromic acid and chromic-phosphoric acid.

6. A blackened, corrosion-resistant ferrous metal surface prepared in accordance with the method of claim 4.

7. A blackened, corrosion-resistant ferrous metal surface prepared in accordance with the method of claim 5.

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