METHOD FOR PRODUCING BLACK COATINGS ON METAL SURFACES

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ABSTRACT OF THE DISCLOSURE

Black matte coatings which are uniform in appearance and thickness and stable under relatively severe wear conditions are produced on metal surfaces by treating the surface with an aqueous acidic solution of a trivalent antimony salt and then depositing a protective coating, preferably a phosphate coating, thereon. The coating is somewhat darker if the phosphate solution contains nickel, and the antimony-containing solution remains homogeneous over longer periods of time if it contains a small amount of a stannous salt.

This invention relates to coatings for metal surfaces and more particularly to a new method for producing a black matte finish on a metal object, which method comprises contacting the surface of said object with an aqueous acidic solution of a trivalent antimony salt and thereafter depositing a protective coating thereon.

The provision of a black coating of uniform appearance for metal articles is of increasing importance, especially in the automobile industry. Certain automobile manufacturers now require that parts furnished to them have such a coating. The difficulty has been that uniform black coatings have not been capable of simple production. The methods hereinafter described have involved paints, pigmented oils or additives to metal treatment baths (e.g., phosphating baths). Each of these is attended by serious disadvantages such as non-uniformity in appearance or coating thickness, "smudging," evolution of flammable solvent fumes, and low resistance to abrasion and wear.

A principal object of the present invention, therefore, is to provide an improved method for producing black coatings on metal surfaces.

A further object is to provide a method for blackening metal surfaces which is simple to use and compatible with a wide variety of metal treatment procedures.

A still further object is to produce black matte coatings on metal objects, said coatings being uniform in appearance and thickness and stable under relatively severe wear conditions.

Other objects will in part be obvious and will in part appear hereinafter.

The method of this invention may be used with any metal which will receive a phosphate coating. These include ferrous metals, cadmium, zinc and aluminum. The method is particularly advantageous on ferrous metal surfaces.

As indicated above, the method of this invention involves an initial treatment of the metal object being coated with an acidic solution of a trivalent antimony salt. Any of the water-soluble salts of trivalent antimony are satisfactory for this purpose; however, antimony trichloride is preferred. Based on the chloride, the concentration of antimony salt in the solution should be about 0.3—10.0 grams per liter, and preferably about 0.5—3.1 grams per liter.

The acid should be one which does not react violently or passivate the surface of the metal being treated or oxidize the antimony salt. Thus, neither sulfuric or nitric acids are suitable for use, since each of these acids oxidizes trivalent to pentavalent antimony. Furthermore, nitric acid passivates the surface of steel. In general, a strong mineral acid is desired, and hydrochloric acid is generally convenient and suitable. The concentration of hydrochloric acid in the solution is preferably about 25—80 grams per liter. If lower acid percentages are used, insoluble antimony oxychloride may form and precipitate, while if higher percentages are used, uniformity of the black coating is impaired.

The presence of a stannous compound in the antimony salt solution is often beneficial, since stannous salts seem to retard the precipitation of antimony trioxide. About 0.3—0.4 gram of stannous chloride per gram of antimony trichloride is sufficient to accomplish this purpose.

According to this invention, the metal object is first thoroughly cleaned and is then contacted with the antimony-containing solution (e.g., by immersion or spraying) for a period of time sufficient to provide a black coating of the desired thickness. The preferred time is in the range of about 20—70 mg. per square foot, preferably about 50 mg. per square foot. The time required to form a coating of this thickness is usually between about 10 seconds and about 4 minutes. For a 50 mg. per square foot coating, about 2 minutes is suitable. The temperature of the antimony treatment is preferably about room temperature (e.g., 70—80°F.).

Following treatment with the antimony solution, the metal object may be rinsed with water or another suitable rinsing medium; this rinsing step is desirable but not necessary. The object is then coated with a protective coating.

Protective coatings suitable for use in the method of this invention are of many types and include, for example, lacquers, plastic coatings, phosphate coatings and chromate conversion coatings. The phosphate coatings are preferred, they being prepared by contacting the surface of the object with an aqueous acidic solution containing phosphate ions, usually in combination with auxiliary ions such as zinc, manganese, lithium, beryllium, magnesium, calcium, strontium, cadmium, barium and nickel. The presence of antions such as nitrate, chloride, ferrocyanide, ferricyanide or the like is also advantageous.

The composition of the phosphating solution is not critical, but excellent results are obtained with solutions described in U.S. Patent 3,090,709 and in copending application Ser. No. 323,134, filed Nov. 12, 1963. These solutions generally contain as essential ingredients the phosphate ion, either zinc or nickel ion and at least one other metal nitrate from the group listed above. Zinc, if present, usually comprises about 0.1—0.4% (by weight) of the solution, and nickel may comprise about 0.005—2.0% thereof. Nickel-containing solutions are especially desirable since the presence of nickel ion reduces the "smudging" tendency of the blackened surface. The presence in the phosphating solution of small amounts of antimony, due to "drag-out" from the pre-dip solutions, is not harmful and in some instances may increase the thickness of the black coating.

The following table gives the compositions of several phosphating solutions which may be used in the method of this invention. All figures represent weight percentages of the various ions except for "points total acid," which denotes the number of milliliters of 0.1 N aqueous sodium hydroxide required to neutralize a 10 ml. sample of the solution, using phenolphthalein as an indicator. The examples given are not to be considered as limiting the
The preparation of some of the phosphating solutions in the above table is effected in the following manner.

**Example 1**

To 24.6 grams of water there are added 1.4 grams of lime (72% calcium oxide) and 11.7 grams of 75% commercial phosphoric acid. The solution is then diluted by dissolving 4 parts (by volume) in 100 parts (by volume) of water. To 1 liter of the diluted solution there is added 0.25 gram of sodium nitrite and 2 grams of nickel nitrate hexahydrate.

**Example 2**

To 87.3 grams of water there are added 11.7 grams of lime (72% calcium oxide), 68.4 grams of 75% commercial phosphoric acid, and 12.6 grams of nickel nitrate hexahydrate. This concentrate, having a specific gravity of 1.3, is diluted by dissolving 2 parts (by volume) in 100 parts (by volume) of water.

**Example 3**

This solution is prepared by dissolving 2.3 grams of lime (72% calcium oxide), 10.7 grams of 75% commercial phosphoric acid, 2.4 grams of nickel nitrate hexahydrate, 4.3 grams of 42% Baumé nitric acid, and 10 grams of ammonium dihydrogen phosphate in 970 grams of water.

**Example 4**

To 830 grams of water there are added 121 grams of 75% commercial phosphoric acid, 15 grams of 42% Baumé nitric acid, 18 grams of lime (72% calcium oxide) and 16 grams of nickel nitrate hexahydrate.

**Example 5**

An aqueous solution (1 liter) is prepared containing 4.98 grams of zinc nitrate, 6.88 grams of ammonium dihydrogen phosphate and 6.32 grams of calcium nitrate trihydrate.

**Example 6**

An aqueous solution (one liter) is prepared containing 14.2 grams of zinc nitrate hexahydrate, 7.8 grams of 75% phosphoric acid, 4.2 grams of zinc chloride, 8.7 grams of ammonium dihydrogen phosphate, and 14.3 grams of calcium nitrate trihydrate.

**Example 10**

A concentrate is prepared from 31 grams of 75% phosphoric acid, 26.3 grams of 67% nitric acid, 12.9 grams of zinc oxide, 12.0 grams of ammonium dihydrogen phosphate, 3.7 grams of 50% sodium hydroxide, and 14.1 grams of water. This concentrate is diluted with water to 3% (by volume).

**Example 11**

A concentrate is prepared from 65.4 grams of an aqueous solution containing 20.95% (by weight) zinc oxide and 31.2% nitric acid, 16.0 grams of 75% phosphoric acid, and 18.6 grams of ammonium dihydrogen phosphate.
containing 42.8 grams per liter of SbCl₃ and 500 ml. per liter of 38% HCl.

**Example 15**

A continuous operation similar to that of Example 14 is conducted, except that the antimony solution also contains 0.25 gram per liter of stannous chloride. It is found that the bath remains homogeneous during the treatment of a considerably greater total surface area of metal.

**Example 16**

The procedure of Example 14 is repeated, using an antimony solution containing 0.67 gram per liter of SbCl₃ and about 43.4 grams per liter of HCl, and the phosphate bath of Example 11. A similar procedure is followed using the nickel-containing phosphate bath of Example 12. The latter is found to produce a somewhat darker coating.

What is claimed is:

1. A method for producing a black matte finish on a ferrous metal, zinc, cadmium or aluminum object which comprises contacting the surface of said object with an aqueous acidic solution of a trivalent antimony salt, the acid in said solution being one which does not react violently with or passivate the metal surface or oxidize said antimony salt, and thereafter depositing a phosphate conversion coating on said surface.

2. The method of claim 1 wherein the phosphate coating is applied by contacting the metal surface with an aqueous acidic solution containing as essential ingredients the phosphate ion and one or both of zinc and nickel ions, the zinc comprising about 0.1–1.36% by weight of said solution and the nickel about 0.005–2.0% thereof.

3. The method of claim 2 wherein the phosphate solution contains nickel ion.

4. The method of claim 2 wherein the metal surface is a ferrous metal.

5. The method of claim 4 wherein the antimony salt is antimony trichloride and the acid used in the antimony-containing solution is hydrochloric acid.

6. The method of claim 5 wherein the concentration of antimony salt in the antimony-containing solution is about 0.3–10.0 grams per liter and the concentration of HCl therein is about 25–80 grams per liter.

7. A method according to claim 6 which comprises (A) contacting the surface of said object with said antimony salt solution; (B) thereafter contacting said surface with an aqueous acidic solution containing as essential ingredients the phosphate ion and one or both of zinc and nickel ions, the zinc comprising about 0.1–1.36% by weight of said solution and the nickel about 0.005–2.0% thereof; and (C) treating said surface with one or both of (1) an aqueous chromate or chromic acid solution and (2) a complex metal salt of a phosphoric acid ester.

8. The method of claim 7 wherein the antimony trichloride solution also contains a stannous salt, about 0.3–0.4 gram of said stannous salt, calculated as stannous chloride, being present per gram of antimony trichloride.

9. A ferrous metal, zinc, cadmium or aluminum object carrying on its surface a black matte coating applied by the method of claim 1.

10. A ferrous metal object carrying on its surface a black matte coating applied by the method of claim 4.

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