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PHOSPHATE COATING OF METALLIC ARTICLES

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1 Claim. (Cl. 148—6.15)

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The invention described herein may be manufactured and used by or for the Government for governmental purposes, without the payment to me of any royalty thereon.

This invention relates to phosphate coating of metallic articles and more particularly to a method of producing greatly improved phosphate coatings. This invention has application in the field in which rustproof coatings of metallic phosphates are formed upon articles having a surface of iron, zinc, cadmium, magnesium, aluminum, and alloys thereof by immersing the article in an acidic aqueous solution comprising metallic phosphates, such as ferrous phosphates and metallic phosphates selected from the group consisting of zinc phosphates, manganese and copper phosphates.

I have found that improved coatings are produced as a result of adding to the phosphate coating bath a compound of boron, which will liberate boric acid in the bath at a relatively slow rate. I prefer to use a metallic fluoborate, boron phosphate or fluoboric acid.

It is a characteristic of the boron compounds which I desire to use that they hydrolyze relatively slowly in phosphate coating baths to yield boric acid. As distinguished from this, the borates hydrolyze very rapidly to give boric acid, and hence are undesirable for employment in accordance with the invention.

It is known that additions of boric acid to phosphate coating baths result in improvement in the finishes produced upon metallic articles treated in the bath. However, the addition of boric acid is accompanied by many undesirable results. The baths are operated at elevated temperatures slightly below the boiling point, and, at these temperatures, the boric acid is rapidly lost from the bath by volatilization or steam distillation; hence its beneficial effects are short lived. Because of the rapid loss of boric acid, frequent replenishment is necessary.

The invention will be more particularly described in reference to the coating of ferrous metals utilizing a bath containing ferrous phosphates, zinc phosphates and a nitrate. It will be understood, however, that this is by way of example only and is not to be construed as limiting the invention.

The following table gives the characteristics of

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a typical and satisfactory phosphate coating bath:

Free acidity	points	4.0
Total acidity	do	25
Proportion of total to free acid		1–6.25
Iron	percent	0.40
Zinc	do	0.35
Nitrate	do	2.5

The free acidity is measured in conventional manner by titrating 10 cc. sample of the bath with 0.1 N sodium hydroxide to the methyl orange end point; the number of ccs. of sodium hydroxide required is the point value of the free acidity. The total acidity is determined by titrating a 10 cc. sample of the bath with 0.1 N sodium hydroxide using phenolphthalein indicator; the number of ccs. of sodium hydroxide required is the point value of the total acidity. Iron, zinc and nitrate are determined by conventional quantitative analytical methods.

The bath described immediately above when operated at a temperature of from 205° F. to 210° F. produced a satisfactory coating on a steel article immersed in the solution for a period of one-half hour.

To the bath described above, which had a volume of 270 gallons, was added one pint of an aqueous solution of zinc fluoborate having the following analysis:

	Percent
$Zn(BF_4)_2$	47.55
Free HBF_4	0.52
Free H_3BO_3	4.11

After the addition of the solution of zinc fluoborate to the bath, a steel article was treated therein for a period of one-half hour. The article was found to be coated with a much darker almost black film exhibiting a uniformly fine crystalline structure. Such article showed improved corrosion resistance as compared to the article similarly prepared in a bath containing no zinc fluoborate.

It has been found that quantities of fluoborate greater than one pint of zinc fluoborate in 270 gallons of phosphating solution do not materially improve the quality of the coating produced. However, the effect of the addition extends over a longer period of time. For example, the effects of

one pint of fluoborate may last for three to four days and the effects of the addition of two pints may last from six to eight days. Even very large additions of zinc fluorborate up to as much as four or five gallons per 270 gallons of phosphate bath do not have any deleterious action. Such large additions will result in improved coating action for a relatively extended period of time.

It is believed that the zinc fluorborate hydrolyzes in the acid bath to yield boric acid, zinc fluoride and hydrofluoric acid in accordance with the following equation:

$$Zn(BF_4)_2+6H_2O \overset{[H^+]}{\rightleftarrows} 2H_3BO_3+ZnF_2+6HF$$

The formation of the zinc fluoride and the hydrofluoric acid is believed to add to the effectiveness of the bath by reducing the temperature at which the bath may be operated for the production of a superior coating.

Other metallic fluoborates may be employed in a manner similar to that described for the employment of zinc fluoborate. Manganese fluoborate [$Mn(BF_4)_2$] may be advantageously used in phosphating baths containing a mixture of ferrous and manganese phosphates. Where copper is used in the coating bath, additions of copper fluoborate have been found to produce better coatings. Fluoboric acid may be employed if desired. Boron phosphate [BPO_4] also may be used to advantage in any of the phosphating baths. It has been found that additions of from one-half pound to three pounds of boron phosphate to 240 gallons of a zinc-ferrous phosphating bath as set forth above will condition the bath with a production of superior coatings for a period of from four days to three weeks.

It is believed that boron phosphate hydrolyzes to yield boric acid and phosphoric acid in accordance with the following:

$$BPO_4+3H_2O \overset{[H^+]}{\rightleftarrows} H_3BO_3+H_3PO_4$$

Because the addition of boron phosphate to the coating bath has a tendency to raise the free acid value of the bath, boron phosphate can be used to advantage as an addition agent where the free acidity is lower than desired.

I claim:

The process for forming a rustproofing coating of a metallic phosphate upon a ferrous metal surface which comprises subjecting said surface to the action of an aqueous solution the solutes of which consist essentially of free phosphoric acid, a phosphate of a metal selected from the group consisting of zinc, manganese and copper, and boron phosphate in the proportion of about one-half pound to about three pounds per about 240 gallons of said solution.

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