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CHLORATE ACCELERATED ZINC PHOSPHATING BATHS WITH ADDED ARSENATE

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This invention is directed to compositions for depositing zinc phosphate coatings on steel and galvanized steel and to processes of using the compositions to coat steel and galvanized steel. More particularly, this invention is directed to chlorate accelerated zinc phosphating solutions containing a small amount of arsenate and to processes for using these solutions in the coating of steel and galvanized steel.

The addition of a phosphate coating to steel or galvanized steel provides increased resistance against corrosion and greater adhesion for decorative coatings, as compared to uncoated metal. Moreover, phosphate coatings on steel, when combined with lubricants, facilitate the cold forming of metals.

Zinc phosphate solutions accelerated with chlorate ion are notoriously unpredictable. These solutions will deposit good coatings on steel when freshly prepared but after an unpredictable time, the quality of the coating deteriorates and the bath becomes unusable. This time period may be as short as several hours, and if a large bath of several thousand gallons must be discarded, considerable loss takes place.

I have discovered that if a small amount of arsenate is added to a bath which has deteriorated in its ability to deposit satisfactory coatings, the efficient coating characteristics of the bath can be quickly restored. Alternatively, if a small quantity of arsenate is added to the bath initially and provided this concentration is maintained in solution during operation of the bath, efficient phosphate coating can be obtained indefinitely on steel and galvanized steel.

The minimum quantity of arsenate ion required to restore a chlorate accelerated zinc phosphating solution to efficient operation or to be incorporated initially to assure long continued satisfactory operation is as low as 0.01 gram/liter. Higher concentrations can be used and concentrations of 1.0 gram/liter will also give efficient and satisfactory phosphate coatings. It is preferred that the arsenate be within the range of 0.02 to 0.15 gram/liter in the coating bath.

The arsenate ions may conveniently be supplied by arsenic acid or its water soluble salts such as NA_2HAsO_4, NaH_2AsO_4, Na_3AsO_4. The hydrates of these salts are equally satisfactory. Similarly, water soluble arsenous acid salts which will oxidize in the presence of the chlorate to the arsenate are equally satisfactory. An example of this type is sodium arsenite, $NaAsO_2$. Certain arsenic oxides, such as the trioxide and pentoxide, which react with water under the oxidizing presence of the chlorate to form arsenate ions are also satisfactory. The arsenate can be added to the liquid concentrates which are diluted with water to form the coating bath or the arsenate may be added directly to the coating bath. Preferably, it is added to the concentrate.

The aqueous zinc phosphating solutions are sold commercially in the form of liquid concentrates to avoid unnecessary shipping charges for water. The concentrates for making zinc phosphate solutions are conveniently prepared from phosphoric acid, zinc oxide and water, to which is added the necessary small amounts of chlorate accelerator and arsenate additive.

In preparing the liquid concentrates generally zinc oxide or zinc carbonate is reacted with excess aqueous

phosphoric acid under controlled conditions of agitation and temperature. It is desired to put as much as possible of zinc into solution. However, practical limits are encountered since deposition of solids due to low temperatures which may be encountered in shipping or warehousing must be avoided. Generally, concentrates are formulated so that little or no solids will deposit at —10° F.

The chlorate may be added to the concentrate as sodium chlorate or as potassium chlorate. The amount of chlorate in the concentrate is regulated so that upon dilution for use the chlorate is within the range of 0.5 to 15 grams/liter. Preferably, the chlorate concentration is between 2 and 10 grams per liter in the coating bath. If necessary, the chlorate may be added directly to the bath.

The aqueous concentrate generally comprises zinc ions, phosphate ions, arsenate ions and chlorate ions. These ions will be present in relative proportions by weight so that the concentrates will be ready for use merely by diluting with water. Generally the aqueous concentrates comprise zinc, phosphate, chlorate and arsenate in the following range of percentages by weight:

	Percent
Zinc	5 to 10
Phosphate	15 to 30
Chlorate	8 to 16
Arsenate	0.1 to 0.2

It will be appreciated that the balance of the concentrate will be partly water and the corresponding anions or cations of the compounds used to make the concentrate.

The concentrate may also contain as much as ten percent by weight nitrate added as nitric acid, zinc nitrate, nickel nitrate or alkali metal nitrates.

When it is desired to use the concentrate to coat both steel and galvanized steel, the concentrate may contain as much as 4% by weight nickel. The nickel may be added as nickelous nitrate, nickelous carbonate or nickelous oxide. The nitrate and the nickel may be added either to the concentrate or to the coating bath.

A typical liquid concentrate can be made from phosphoric acid (75%), 29.8%; zinc oxide, 9.3%; sodium chlorate, 13.4%; nitric acid (60%), 6.8%; disodium arsenate, 0.2%; water, 40.5%, with percentages given as weight percent.

The above liquid concentrate may be diluted at the ratio of thirty-five pounds to one hunderd gallons of water. After dilution in water is effected, the acid ratio is checked and corrections made by the addition of zinc oxide, zinc carbonate, phosphoric acid, nitric acid, etc. The bath operating temperature is generally maintained between about 130 to 180° F.

It is desirable that the total acid value be at least about 6 points and that the acid ratio of the use solutions be controlled within the range of 4:1 to 15:1 depending on the temperature of the bath. At a temperature of about 180° F. the acid ratio is about 4:1 whereas at 130° F. the acid ratio is preferably at 15:1 The acid ratio is the ratio of total acid points to free acid points. The acid ratio is determined by standard titration procedures wherein a 10 ml. sample of the test solution is titrated with 0.1 normal sodium hydroxide. The total acid point value is the number of milliliters of 0.1 N sodium hydroxide required to reach the end point using phenolphthalein indicator, whereas the free acid point value is determined by using bromphenol blue indicator.

It will be appreciated that the acid ratio can be adjusted by the addition of acid such as phosphoric (75%) or by such acids as nitric or hydrochloric acid. Similarly, the acid ratio can be adjusted by the addition of

alkaline materials such as zinc oxide or zinc carbonate. Small amounts of sodium hydroxide can be used to adjust the acid ratio although this material is not preferred.

Where it is desired to coat galvanized steel, it is preferable to include a soluble nickel compound in the coating bath. The amount of nickel in the operating bath should be at least 0.1 gram/liter and a useful range of soluble nickel is 0.1 to 7 grams/liter in the operating bath. A preferred range is 0.3 to 1.5 grams/liter of nickel.

The coating bath will generally contain 0.5 to 10 grams/liter of zinc ions and 2 to 20 grams/liter of phosphate ions. Preferably the zinc ion content will be 1 to 7 grams/liter while the phosphate will be 4 to 20 grams/liter.

Nitrate ion may be present to improve the coating characteristics of the bath in the concentration range of 0.5 to 20 grams/liter.

The steel or galvanized steel must be thoroughly cleaned prior to phosphating. Cleaning may be effected by use of alkaline cleaners or by vapor degreasing or by a combination of both. An alkaline cleaner particularly suitable for spray application contains tetrasodium phosphate and wetting agent. If an activated cleaner is desired, the cleaner will contain about 10% of activating salts. Activated cleaners are desired for the production of faster and more dense phosphate coatings. The cleaner may be applied at 160° F. A one minute spray cleaning followed by a one-half minute water rinse is usually satisfactory for precleaning. Vapor degreasing may be accomplished by the use of trichloroethylene or perchloroethylene when desired.

The phosphating solution is preferably applied as a spray and a one-half to one minute application at 130° to 180° F. is usually sufficient for obtaining hard dense coatings on steel or galvanized steel. After application of the phosphate solution, the metal objects are rinsed with water and are usually followed with a chromic acid rinse. This rinse may contain about 0.5 gram/liter of chromic acid and is usually applied at 150° F.

Alternatively, instead of spray application, the phosphate coating may be applied by immersion and in this case the contact time with the solution may vary from ½ to 5 minutes depending on the desired thickness of coating.

The following examples will illustrate the practice of my invention:

Example 1

A zinc phosphate coating concentrate was prepared from the following materials:

	Percent by weight
Phosphoric acid, 75%	29.8
Zinc oxide	9.3
Sodium chlorate	13.4
Nitric acid, 60%	6.8
Water	40.7

Thirty-five pounds of this solution was diluted to 100 gallons with water and heated to 150° F. Ten ounces of zinc carbonate was added to adjust the acid ratio to provide a solution approximately saturated with respect to zinc phosphate. Under these conditions the bath had an acid ratio of 8:1 and a total acid point value of about 14.

On clean steel, this bath when applied by spraying for one minute produced hard adherent coatings. However, after the bath had been used for about four hours, the coatings became soft, and were generally unsatisfactory.

Example 2

A zinc phosphate coating concentrate was prepared the same as given in Example 1, but 0.2% by weight of anhydrous disodium arsenate was incorporated and the amount of water reduced by 0.2%. This solution was used to prepare a coating bath in exactly the same manner as in Example 1. This bath produced satisfactory hard adherent coatings on steel over a prolonged period of many months.

Example 3

For application of zinc phosphate coatings to steel and galvanized steel simultaneously, it is desirable to incorporate in the coating bath a nickel salt. This improves the quality of the coating formed on galvanized steel.

A suitable concentrate was prepared by combining the following ingredients:

	Percent by weight
Phosphoric acid, 75%	41.0
Zinc oxide	8.3
Sodium chlorate	10.8
Nickelous nitrate, hexahydrate	9.1
Disoduim arsenate, anhyd.	0.25
Water	30.55

A bath having a total acid value of 13 to 15 points prepared from this concentrate deposited hard, adherent coatings on both steel and galvanized steel for an extended period of many months.

Example 4

A bath similar to that of Example 3 was prepared, but without the disodium arsenate. This bath initially formed good coatings on steel and galvanized steel, but after a short time the coatings on steel become soft and non-adherent.

The foregoing description and examples of my invention are illustrative only and are not intended to limit my invention other than as defined in the following claims.

Example 5

The concentrate of Example 2 was diluted with water to form a coating solution having the following concentrations expressed in grams per liter:

Zinc	0.745
Phosphate	2.16
Nitrate	0.402
Chlorate	1.05
Arsenate	0.015

Good coatings were obtained on steel by spraying for one minute at 175° F.

Example 6

The concentrate of Example 3 was diluted with water to form a coating solution having the following concentrations expressed as grams per liter:

Zinc	6.65
Phosphate	29.7
Nitrate	3.9
Chlorate	8.5
Arsenate	0.19
Nickel	1.84

This solution was used to spray coat steel and galvanized steel by application for one minute at 180° F. Hard adherent coatings were obtained for a period extending over several months.

I claim:

1. The aqueous zinc phosphating solution for coating steel comprising at least 0.5 gram per liter of zinc ions, at least 2 grams per liter of phosphate ions, at least 0.5 gram per liter of chlorate ions and at least 0.01 gram per liter of arsenate ions.

2. The aqueous zinc phosphating solution for coating steel comprising 0.5 to 10 grams per liter of zinc ions, 2 to 20 grams per liter of phosphate ions, 0.5 to 15 grams per liter of chlorate ions, and 0.01 to 1.0 gram per liter of arsenate ions.

3. The aqueous zinc phosphating solution for coating steel of claim 2 having a total acid value of at least

about 6 points and an acid ratio within the range of 4:1 to 15:1.

4. The phosphating solutions of claim 2 including 0.1 to 7 grams per liter of nickel ions for coating steel and galvanized steel.

5. The phosphating compositions of claim 2 including 0.3 to 1.5 grams per liter of nickel ions for coating steel and galvanized steel.

6. The process of phosphating a clean steel surface comprising contacting the clean steel surface with the aqueous solution of claim 2 for a time sufficient to deposit a phosphate coating, removing the steel from contact with the said aqueous solution and thereafter rinsing the steel with water.

7. The aqueous zinc phosphating solution for coating steel comprising 1 to 7 grams per liter of zinc ions, 4 to 20 grams per liter of phosphate ions, 2 to 10 grams per liter of chlorate ions, and 0.02 to 0.15 grams per liter of arsenate ions.

8. The process of phosphating a clean steel surface comprising contacting the clean steel surface with the aqueous solution of claim 7 for a time sufficient to deposit a phosphate coating, removing the steel from contact with the said aqueous solution and thereafter rinsing the steel with water.

9. The aqueous zinc phosphating solution for coating steel comprising 0.5 to 10 grams per liter of zinc ions, 2 to 20 grams per liter of phosphate ions, 0.5 to 15 grams per liter of chlorate ions, and 0.01 to 1.0 grams per liter of arsenate ions, and 0.5 to 20 grams per liter of nitrate ions.

10. The process of phosphating a clean steel surface comprising contacting the clean steel surface with the aqueous solution of claim 9 for a time sufficient to deposit a phosphate coating, removing the steel from contact with the said aqueous solution and thereafter rinsing the steel with water.

11. An aqueous concentrate for preparing zinc phosphating solutions comprising zinc, phosphate, chlorate and arsenate in the range of weight percentages as follows: zinc, 5 to 10; phosphate, 15 to 30; chlorate, 8 to 16; and arsenate, 0.1 to 0.2.

12. The aqueous concentrates of claim 11 which include 1 to 4% by weight of nickel.

13. The aqueous concentrates of claim 11 which include 2 to 10% by weight of nitrate.

14. The liquid concentrate for making aqueous zinc phosphating solutions by dilution with water prepared by combining the following: phosphoric acid (75%), 41.0%; zinc oxide, 9.3%; nitric acid (60%), 6.8%; sodium chlorate, 13.4%; disodium arsenate, 0.2%; water, 40.5%; the said percentages being given as percent by weight.

15. The liquid concentrate for making aqueous zinc phosphating solutions by dilution with water prepared by combining the following: phosphoric acid (75%), 41.0%; zinc oxide, 8.3%; sodium chlorate, 10.8%; nickelous nitrate, hexahydrate, 9.1%; disodium arsenate, 0.25%; water, 30.55%; the said percentages being given as percent by weight.

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