(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 398 202 A1

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: 90108989.6

(22) Date of filing: 12.05.90

(51) Int. Cl.5: C23C 22/12, C23C 22/13, C23C 22/18

(30) Priority: 19.05.89 US 354550

(43) Date of publication of application: 22.11.90 Bulletin 90/47

(84) Designated Contracting States: AT BE DE DK ES FR GB IT NL SE

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(54) **Composition and process for zinc phosphating.**

(57) Sludge generation in zinc phosphating solutions having accelerators other than hydroxylamine can be substantially reduced by adding from 0.02 to 0.4 % by weight of hydroxylamine to the solutions.

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COMPOSITION AND PROCESS FOR ZINC PHOSPHATING

Cross-Reference to Related Application

This application is a continuation-in-part of copending U. S. application Serial No. 06/834,491 filed February 24, 1986, the entire disclosure of which is hereby incorporated herein by reference.

Field of the Invention

This invention relates to an improved process for producing zinc phosphate containing protective layers on the surface of iron, steel, and other metal articles. Such layers, when sufficiently uniform and dense, provide effective substrates for lubrication prior to subsequent drawing or similar metal forming operations. More particularly, this invention relates to treatment solution compositions and processes that reduce the amount of sludge formed during the phosphating operation.

Statement of Related Art

Metal phosphating solutions have been widely used to form coatings on the surfaces of metal articles, particularly those made of iron or carbon steels. Metal phosphating solutions are generally dilute aqueous solutions of phosphoric acid and other chemicals, often including zinc, calcium, and other metal ions, which are contacted with the surfaces of metal by immersion, spraying, or similar means. The surface of the metal reacts with the solution and, under suitable conditions, such reaction fcrms over the surface an integral layer of substantially insoluble crystalline phosphates of various metals, usually including some iron, if that is a part of the metal being phosphated, and some of any metal present as cations in the solution.

The coatings thus formed serve as effective bases for subsequent application of paints, lubricants, and other materials. Such coatings also often resist corrosion, and inhibit corrosion of the underlying metal, in various environments to which metal articles are often exposed in use. Such coatings have achieved widespread commercial use.

One particular area of established use for phosphate coatings is to prepare metal for drawing and other similar forming operations in which reduced surface friction is important. In some such applications, phosphating solutions containing both zinc and calcium cations are established as superior to most if not all others. For example, U. S. Patent 4,688,411 of Aug. 25, 1987 to Hagita et al. teaches use of mixed calcium and zinc phosphate solutions having a calcium to zinc ratio between 0.3 and 1 at 70 - 90° C. As is shown in Figure 4 of this Hagita patent, the higher the ratio of calcium to zinc, the lower is the coating weight achieved during any particular non-zero treating time.

The use of hydroxylamine in phosphating solutions has been known in the art to accelerate the phosphating reaction, thereby increasing the amount of phosphate coating formed under given conditions of treatment from a phosphating solution containing hydroxylamine, compared with an otherwise similar solution not containing hydroxylamine.

In addition to their desired effects, all known phosphating solutions during use generate undesirable material generally known in the art as "sludge", an insoluble mixture of metal phosphates and sometimes other substances that precipitate from phosphating solutions during their use and that must eventually be removed to permit continued satisfactory operation. If the sludge accumulates beyond a certain level, some of it will usually adhere to some of the metal articles being phosphated, thereby making unacceptable surface blemishes on these articles. Disposal of the sludge is costly, because its high concentration of toxic metal ions requires environmental protection measures under current laws. Thus, reduction in the amount of sludge formed during operations is a highly desirable object of improvement in phosphating processes.

Description of the Invention

Except in the operating examples, or where otherwise expressly stated to the contrary, all numbers in this description that specify amounts of materials or conditions of reaction or use are to be understood as modified in all instances by the word "about".

It has been found that satisfactory phosphate coatings for pre-drawing lubricity can be formed in the range of coating weights between 3 and 15 grams per square meter (hereinafter "g/m^2") of surface and that lower coating weights within this range are sometimes preferred, provided that a dense continuous phosphate film is formed. It has also been found that the presence of controlled amounts of hydroxylamine in a zinc phosphating solution, including such solutions that also contain calcium and/or some other metal ions, significantly reduces the formation of sludge during operations, without having any adverse effect on the phosphating process.

One preferred embodiment of the invention is a phosphating solution having a pH in the range of 1 to 3.7, more preferably in the range of 2.5 to 3.5 and comprising, or more preferably consisting essentially of, the following components: (A) from 1 to 4 % by weight of zinc ions; (B) up to 3 % by weight of calcium ions; (C) from 1 to 7.5 % by weight of phosphate ions; (D) at least 0.02 % by weight of hydroxylamine; (E) an accelerator other than hydroxylamine, as known in the art, which may include more than one chemical species, in an accelerating-effective amount; (F) up to 0.1 % by weight of nickel and/or copper cations; (G) up to 0.2 % by weight of manganese cations; and (H) water. In this and the remainder of this specification, any statements of the amount of "phosphate ions" are to be understood as the stoichiometric equivalent as PO_4^{-3} of the sum of all stages of ionization of phosphoric acid and of undissociated acid that may be present in the solutions. Also, it is to be understood that necessarily implied counter-ions, chemically harmless during phosphating, for any constituents stated to be present in ionic form, are also present in the solutions according to the invention.

The preferred accelerator is nitrate ion in an amount between 1 and 7.5 % by weight of the phosphating solution. Other suitable accelerators include, but are not limited to, sulfite ions, picrate ions, vanadates, and/or molybdates.

Within the preferred compositional range stated above, it is more preferred to have the amount of the sum of nickel and copper cations within the range of 0.001 to 0.01 % by weight, with the most preferred value being 0.006 % by weight. If calcium ion is present in the solutions, it is more preferred that it be present in a concentration of at least 0.5 % by weight.

It is preferred to use an amount of hydroxylamine such that an otherwise identical zinc phosphating solution in which all the hydroxylamine has been replaced by an amount of nitrite ion equal to 3 % the weight of the hydroxylamine replaced generates at least 50 % more sludge than the hydroxylamine containing solution for the same amount of metal surface phosphated. It is generally preferred to use not more than 0.4 % by weight of hydroxylamine in the solutions, and the most preferred value for the concentra tion of hydroxylamine is 0.05 % by weight.

Treatment of metal surfaces with hydroxylamine containing phosphating solutions according to this invention may be by immersion, spray, a combination, or any other method that establishes effective contact, and the temperatures, times, and other conditions of treatment are generally the same as those already known in the art for phosphating with solutions containing the same concentrations of the same metal ions and other accelerator(s). Also, the phosphating treatment according to this invention may be advantageously combined with other known process steps, such as pre-phosphating cleaning, pickling, and conditioning procedures and post-phosphating rinses, chromate or other coating passivation treatments, application of lubricants, painting, and the like, all in the general manner well known to those skilled in the art.

Suitable practical and preferred sources for the specified constituents of the phosphating solutions according to this invention are known to those skilled in the art. For example, hydroxylamine is preferably sourced from a shelf-stable salt or complex, several of which are commercially available. Most preferred is hydroxylamine sulfate, sometimes also called hydroxylammonium sulfate and generally represented chemically as $(NH_2OH)_2 \bullet (H_2SO_4)$ or $(NH_3OH)_2SO_4$. Hydroxylamine sulfate is briefly denoted hereinafter as "HAS".

The volume of sludge generated during use of a phosphating solution may be measured by means known to those skilled in the art. Normally, an aliquot sample of the solution is removed from the container in which the process is being performed, with care to assure a representative sample. The aliquot of solution, with its suspended solids, is transferred to a transparent graduated conical vessel and allowed to settle under the influence of ambient gravity for about 24 hours. Such settling produces a readily visible demarcation between the sludge in the bottom of the vessel and the overlying liquid. The volume of sludge is then read from the graduations on the vessel.

Typical phosphating solutions according to this invention generate 7 to 11 milliliters (hereinafter "ml") of sludge per square meter (hereinafter "m^2") of metal phosphated, while conventional zinc phosphate coating solutions generate 14 to 25 ml of sludge per square meter of metal phosphated.

The practice of this invention may be further appreciated by consideration of the following, non-limiting, operating examples.

Examples 1 - 5

These examples illustrate the preparation and use of phosphating solutions according to the present invention. The solutions were made to the compositions shown in Table 1, using zinc oxide as the source of zinc, nitric acid as

Table 1

Compositions of Solutions for Examples 1 - 5					
Component	Percent by Weight of Component in Example:				
	1	2	3	4	5
Zinc ions	1.3	1.7	2.0	2.1	2.7
Calcium ions	1.3	0.9	0.7	0.5	none
Nickel ions	0.006	0.006	0.006	0.006	0.006
Nitrate ions	3.5	3.5	3.5	3.5	3.5
Phosphate ions	3.3	3.3	3.3	3.3	3.3
Hydroxylamine	0.05	0.05	0.05	0.05	0.05
Water formed the balance of the solutions in all cases.					

the source of nitrate ions, phosphoric acid as the source of phosphate ions, calcium hydroxide as the source of calcium ions, nickel nitrate as the source of nickel ions, and HAS as the source of hydroxylamine. Some results of using these solutions are shown in Table 2.

Examples 6 - 7 and Comparative Examples 1C - 3C

The compositions of solutions for these examples is shown in Table 3. The same sources of the components as in Examples 1 - 5 were used, and sodium nitrite was used as the source of nitrite ions.

Table 2

Coating Weights and Sludge Volumes for Examples 1-5		
Example No.	Coating Weight Range, g/m^2	Sludge Volume, ml/m^2
1	3 - 5	10
2	8 - 10	10
3	9 - 13	11
4	12 - 15	10
5	12 - 20	9

Table 3

Compositions of Solutions for Examples 6 - 7 and 1C - 3C					
Component	Percent by Weight of Component in Example:				
	6	1C	2C	3C	7
Zinc ions	1.5	3.0	1.9	1.2	1.2
Calcium ions	0.8	none	none	1.2	1.2
Nickel ions	0.006	0.006	0.006	0.006	0.006
Nitrate ions	4.3	3.6	2.9	4.7	4.7
Phosphate ions	3.4	3.4	0.6	3.2	3.2
Hydroxylamine	0.05	none	none	none	0.05
Nitrite ions	none	.0015	.0015	.0015	none

The comparative examples are all solutions known from prior art. Comparative Example 1C is a traditional zinc solution for high coating weight phosphating and 2C is a conventional solution for low coating weight phosphating, both of these having no calcium. Comparative Example 3C contains calcium but is otherwise fairly close to 1C. All these comparative examples contain nitrite as an accelerator, along with nitrate.

Some of the results obtained with these solutions are shown in Table 4. Example 7 used a solution that is identical with that for Comparative Example 3C, except that the hydroxylamine in the solution of Example 7 has been replaced in the solution of Comparative Example 3C by nitrite ion; the amount of nitrite ion used is 3 % by weight of the amount of hydroxylamine substituted. The phosphating coating weight and quality produced by the two solutions is substantially identical, but the amount of

Table 4

Coating Weights and Sludge Volumes, Examples 6-7 and 1-3C		
Example No.	Coating Weight Range, g/m^2	Sludge Volume, ml/m^2
6	8 - 10	8.4
1C	9 - 14	14
2C	6 - 9	25
3C	4 - 8	14
7	4 - 8	7.9

sludge is over 40 % less for Example 7. Comparison of Example 6 with Comparative Example 1C shows the same general effect for solutions with a higher zinc:calcium ratio.

Example 8

This example describes an integrated process, including use of a phosphating solution according to the present invention, that is very effective in preparing steel tubing or wire for subsequent drawing or cold heading processes.

The steel should be cleaned to assure removal of all grease and oil, generally with the aid of a surfactant as known in the art. After use of a surfactant, the steel is rinsed thoroughly with hot water. If any scale or rust is still detectable on the surface, it should be removed by conventional pickling, preferably in hot inhibited sulfuric or hydrochloric acid. After pickling, the metal must be thoroughly rinsed to prevent too much acidic material from contaminating the phosphating solution. It is advisable to use two water rinses, with the first rinse cold and the second either hot or cold as desired.

After this rinse, the metal in immersed in a phosphating solution according to this invention, maintained at a temperature of about 71 to 93° C, and kept in the solution for about 30 seconds to about 5 minutes in order to produce the desired coating. The optimum coating weight depends on the exact composition of the metal being treated, the pretreatment steps, and the type of subsequent processing to be performed on the treated metal, in a manner generally known to those skilled in the art.

In one highly preferred embodiment, the phosphating solution is made by combining separate make-up and additive solutions in a stainless steel processing tank. In a typical installation, 100 gallons of working solution is made by filling the tank about three-quarters full with water and then adding 12.2 gallons of a make-up solution with a composition as specified below. Then about 3.7 gallons of additive solution, with composition specified below, is added to complete preparation of the phosphating mixture.

The make-up solution for this highly preferred embodiment consists of 87.5 parts of zinc oxide, 2.3 parts of nickel nitrate aqueous solution containing 13.7 % by weight of nickel ions, 211.0 parts of 75 % aqueous phosphoric acid, 6.0 parts of HAS, and 113 parts of nitric acid of 42° Baume, all dissolved in sufficient water to make 1000 parts total. The additive solution is made by mixing 261.7 parts of calcium hydroxide and 665.4 parts of nitric acid of 42°. Baume, with sufficient water to make 1000 parts total. (All parts noted in this paragraph are by weight.)

After the phosphate coating has been applied, the treated article is rinsed well to remove, and prevent any carryover of, the phosphating solution. A suitable lubricant is then applied from an aqueous soap solution. The article is then ready for drawing or other forming operations that substantially stress the metal.

During the operation of the process, some sludge accumulates. This should be removed regularly before it builds to a sufficient amount to cause blemishes on the coatings. Also, the solution concentration changes with continued use, and more additive solution as described above is added to the phosphating solution at appropriate intervals to compensate for this depletion of some of the original ingredients.

Claims

1. An aqueous composition suitable for phosphating metal surfaces, having a pH in the range of about 1 to about 3.7 and comprising (A) at least about 1 % by weight of zinc ions; (B) up to about 3 % by weight of calcium ions; (C) at least 1 % by weight of phosphate ions; (D) at least 0.02 by weight of hydroxylamine; (E) an accelerator, other than hydroxylamine, in an accelerating-effective amount; (F) up to about 0.1 % by weight of cations selected from nickel and copper cations; (G) up to about 0.2 % by weight of manganese cations; and (H) water, said aqueous composition having the characteristic that if another composition, designated the substitute composition, that is identical to said aqueous composition except for the substitution of all the hydroxylamine content of said aqueous composition by nitrite ion in an amount of about 3 % by weight of the hydroxylamine substituted, is compared with said aqueous composition by measuring the amount of sludge generated by equal volumes of each composition during phosphating of equal surface areas of the same kind of metal under identical conditions, including a phosphating temperature in the range of about 71 - 93° C, the volume of sludge generated by the substitute composition is at least 50 % greater than the volume of sludge generated by said aqueous composition.

2. An aqueous composition according to claim 1, comprising at least about 0.001 % by weight total of ions selected from the group of nickel and copper cations.

3. An aqueous composition according to claim 2, having a pH in the range of about 2.5 to about 3.5 and comprising from about 1 to about 4 % by weight of zinc ions; from about 1 to about 7.5 % by weight of phosphate ions; from about 0.02 to about 0.4 % by weight of hydroxylamine; and from about 1 to about 7.5 % by weight of nitrate ions.

4. An aqueous composition according to claim 1, comprising from about 1 to about 4 % by weight of zinc ions; from about 1 to about 7.5 % by weight of phosphate ions; from about 0.02 to about 0.4 % by weight of hydroxylamine; and from about 1 to about 7.5 % by weight of nitrate ions.

5. An aqueous composition according to claim 4, comprising about 0.5 to about 3 % by weight of calcium ions.

6. An aqueous composition according to claim 3, comprising about 0.5 to about 3 % by weight of calcium ions.

7. An aqueous composition according to claim 6, comprising about 0.05 % by weight of hydroxylamine.

8. An aqueous composition according to claim 5, comprising about 0.05 % by weight of hydroxylamine.

9. An aqueous composition according to claim 4, comprising about 0.05 % by weight of hydroxylamine.

10. An aqueous composition according to claim 3, comprising about 0.05 % by weight of hydrox-

ylamine.

11. In a process for phosphating a metal by contacting said metal with an aqueous composition having a pH in the range of about 1 to about 3.7 and comprising zinc ions, phosphate ions, an accelerator other than hydroxylamine, and water, the improvement wherein said aqueous composition also contains at least about 0.02 % by weight of hydroxylamine and is characterized by the fact that, if another composition, designated the substitute composition, that is identical to said aqueous composition except for the substitution of all the hydroxylamine content of said aqueous composition by nitrite ion in an amount of about 3 % by weight of the hydroxylamine substituted, is used for phosphating under the conditions of said process and the volume of sludge generated by equal volumes of each composition during phosphating of equal surface areas of the same kind of metal is measured, the volume of sludge generated by the substitute composition is at least 50 % greater than the volume of sludge generated by said aqueous composition.

12. A process according to claim 11, wherein said aqueous composition also contains at least about 0.001 % by weight of ions selected from the group consisting of nickel and copper cations.

13. A process according to claim 12, in which said aqueous composition has a pH within the range of about 2.5 to about 3.5 and comprises from about 1 to about 4 % by weight of zinc ions; from about 0.001 to about 0.01 % by weight total of ions selected from nickel and copper cations; from about 1 to about 7.5 % by weight of phosphate ions; from about 0.02 to about 0.4 % by weight of hydroxylamine; and from about 1 to about 7.5 % by weight of nitrate ions.

14. A process according to claim 11, in which said aqueous composition has a pH within the range of about 2.5 to about 3.5 and comprises from about 1 to about 4 by weight of zinc ions; from about 0.001 to about 0.01 % by weight total of ions selected from nickel, copper, and manganese cations; from about 1 to about 7.5 % by weight of phosphate ions; from about 0.02 to about 0.4 % by weight of hydroxylamine; and from about 1 to about 7.5 % by weight of nitrate ions.

15. A process according to claim 14, in which said aqueous composition comprises about 0.5 to about 3 % by weight of calcium ions.

16. A process according to claim 13, in which said aqueous composition comprises about 0.5 to about 3 % by weight of calcium ions.

17. A process according to claim 16, in which said aqueous composition comprises about 0.05 % by weight of hydroxylamine.

18. A process according to claim 15, in which said aqueous composition comprises about 0.05 % by weight of hydroxylamine.

19. A process according to claim 14, in which said aqueous composition comprises about 0.05 % by weight of hydroxylamine.

20. In a process for phosphating a metal by contacting said metal with an aqueous composition having a pH in the range of about 1 to about 3.7 and comprising zinc ions, phosphate ions, an accelerator other than hydroxylamine, and water, the improvement wherein said phosphating process generates less than about 13 ml of sludge per square meter of metal surface phosphated.

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EUROPEAN SEARCH REPORT

Application number

EP 90108989.6

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl.⁵)
X	EP - A1 - 0 315 059 (PARKER CHEMICAL CO.) * Claims 1,3-5,14,18,21,22; examples *	1-4,9,10	C 23 C 22/12 C 23 C 22/13 C 23 C 22/18
X	DE - A1 - 3 543 733 (PARKER CHEMICAL CO.) * Claims 1,3-9; examples *	1-4,9,10	
A	EP - A1 - 0 155 547 (GERHARD COLLARDIN GMBH) * Claims 1-3,5 *	1	
A	US - A - 4 793 867 (CHARLES et al.) * Claims; examples; column 4, line 64 - column 5, line 8 *	1-4,9,10	

TECHNICAL FIELDS SEARCHED (Int Cl.⁵)

C 23 C 22/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	22-08-1990	PUSTERER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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