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

(11) Publication number: 0 056 675
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 82200062.6

(22) Date of filing: 19.01.82

(51) Int. Cl.^{3}: C 23 F 7/10

(30) Priority: 19.01.81 JP 7028/81

(43) Date of publication of application:
28.07.82 Bulletin 82/30

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

(71) Applicant: Nippon Paint Company, Ltd
2-1-2, Oyodokita Oyodo-ku
Osaka-shi Osaka-fu(JP)

(72) Inventor: Nakatani, Nobuo
c/o Nippon Paint Co. Ltd. 19-17 Ikedanaka-machi
Neyagawa-shi Osaka-fu(JP)

(72) Inventor: Tsuzuki, Tooru
c/o Nippon Paint Co. Ltd. 19-17 Ikedanaka-machi
Neyagawa-shi Osaka-fu(JP)

(72) Inventor: Shimizu, Hideo
c/o Nippon Paint Co. Ltd. 19-17 Ikedanaka-machi
Neyagawa-shi Osaka-fu(JP)

(74) Representative: Green, Alan James et al,
Sanderson & Co. 97 High Street
Colchester Essex C01 1TH(GB)

(54) Pretreatment composition for phosphatising ferrous metals, and method of preparing the same.

(57) An aqueous composition for the treatment of ferrous metal surfaces is a solution comprising:

- (a) titanium compound in amount from 1 to 100 parts per million by weight, measured as titanium;
- (b) phosphate and/or acid phosphate in amount totalling from 50 to 1500 parts per million by weight, measured as PO_4;
- (c) pyrophosphate in amount from 10 to 300 parts per million by weight, measured as P_2O_7; and
- (d) carbonate and/or acid carbonate in amount totalling 20 to 1500 parts per million by weight, measured as CO_3;

the solution having a pH from 8.5 to 9.5.

Croydon Printing Company Ltd

TREATING FERROUS METAL

TITLE MODIFIED
see front page

This invention relates to an aqueous solution for the treatment of ferrous metal surfaces, to the treatment of ferrous metal surfaces with this aqueous solution, to a solid composition suitable for preparing the aqueous solution and to the production of the solid composition.

In the surface treatment of ferrous metals such as steel and other alloys of iron, the usual treatment steps include the following in order: (1) degreasing; (2) washing with water; (3) surface preparation; (4) conversion coating; (5) washing with water; (6) drying; and (7) siccative coating. With respect to the surface preparation step, various proposals have hitherto been made. For example, Japanese Patent Publication Number 7125/1964 discloses the use of a surface preparation composition which is produced by dissolving a titanium oxide with an excess quantity of sulphuric acid, adding thereto phosphoric acid or an alkali metal salt thereof, and/or pyrophosphoric acid or its alkali metal salt to form a slurry at pH of 1 or lower, followed by ageing the slurry at a pH of from 6.5 to 8.5. This surface preparation composition is reported to contribute to the precipitation of the zinc phosphate coating in the conversion coating step which follows. However, when the pH of said composition is about 8.5 or lower, pyrophosphate ion in the composition reacts with the ferrous metal surface to form an iron pyrophosphate coating on the surface thereof, which inhibits the formation of the zinc phosphate coating, thus causing unevenness in treatment. Also, the pH of the surface preparation composition decreases with the passage of time for some unknown reason, and as a result, iron pyrophosphate forms on the surface of the ferrous metals treated with the composition. Furthermore even where the pH of the composition is adjusted to a pH, e.g. about 9, where iron pyrophosphate does not precipitate, such as by the addition of caustic soda, caustic potash, etc., the pH still decreases after a short period of time, causing the problem of iron pyrophosphate coating on the surface of the metals being treated. Accordingly, pH control of this prior art composition is difficult, and satisfactory surface preparations cannot be carried out with the compositions over long periods of time. Frequent replacements of the compositions must be made, with attendant expense and down time, particularly since the usual dipping process involves the use of large quantities of the surface preparation compositions.

In addition to the above problem with the prior art surface preparation composition, this composition does not provide the desired microcrystalline coating in the zinc phosphate conversion coating treatment.

The present invention relates to surface preparation compositions for the treatment of ferrous metal surfaces that do not suffer from the disadvantages of the prior art composition discussed above. The surface preparation compositions of the present invention can be used for long periods of time and such use results in a uniform and dense zinc phosphate coating when a zinc phosphate conversion coating composition is applied to the surface so treated.

The surface preparation compositions of the invention can be used to pretreat any ferrous metal surface, such as steel or other alloys of iron where the alloy consists predominantly of iron.

The invention provides a composition for the treatment of ferrous metal surfaces, which composition is an aqueous solution comprising:

(a) titanium compound in amount from 1 to 100 parts per million by weight, measured as titanium;

(b) phosphate and/or acid phosphate in amount totalling from 50 to 1500 parts per million by weight, measured as PO_4;

(c) pyrophosphate in amount from 10 to 300 parts per million by weight, measured as P_2O_7; and

(d) carbonate and/or acid carbonate in amount totalling 20 to 1500 parts per million by weight, measured as CO_3;

the solution having a pH from 8.5 to 9.5.

Optionally, a rust-inhibiting quantity of nitrite ion, e.g. in the form of its alkali metal salt, such as the sodium or potassium salt, may be added to the solution, provided the quantity added is not so large as to interfere with the effectiveness of the compositions. Additional carbonate and/or acid carbonate may then also be added, if necessary, to keep the pH in the above range.

As sources for the essential ingredients, various compounds may be employed. Examples of such compounds include titanium sulphate or titanium oxide as a source of (a); phosphoric acid, a primary alkali metal salt (e.g. Na or K salt) or primary ammonium salt of phosphoric acid, a secondary alkali metal salt (e.g. Na or K salt) or secondary ammonium salt of phosphoric acid, or a tertiary alkali metal salt (e.g. Na or K salt) or tertiary ammonium salt of phosphoric acid as a source of (b); pyrophosphoric acid or an alkali metal salt (e.g. Na or K salt) or ammonium salt of pyrophosphoric acid as a source of (c); and carbonic acid, an alkali metal salt (e.g. Na or K salt) or ammonium salt of carbonic acid, alkali metal hydrogen carbonate (e.g. Na or K salt) or ammonium hydrogen carbonate as a source of (d).

The present invention also relates to

solid compositions (conveniently in powder form) that can be added to water to form the aqueous pretreatment compositions of the invention. Such solid compositions comprise:

(a) titanium compound in amount from 1 to 100 parts by weight, measured as titanium;

(b) phosphate and/or acid phosphate in amount totalling from 50 to 1500 parts by weight, measured as PO_4;

(c) pyrophosphate in amount from 10 to 300 parts by weight, measured as P_2O_7; and

(d) carbonate and/or acid carbonate in amount totalling 20 to 1500 parts by weight, measured as CO_3.

Optionally, a small quantity of nitrite ion can also be present to provide a rust-inhibiting quantity of nitrite ion when the solid compositions are diluted with a sufficient quantity of water to give the aqueous pretreatment compositions of the invention.

The solid compositions can be prepared by (A) mixing the sources of titanium compound, phosphate and/or acid phosphate, and pyrophosphate together with water in the above proportions; (B) heating the resulting mixture, e.g. at a temperature in the range of from 100° to 120°C until the water content is substantially removed, e.g. to a level of 1.5% by weight or less; and (C) mixing, which should be even mixing, the resulting solid residue with the source of carbonate and/or acid carbonate added in the above proportion.

When ferrous metal surfaces are treated with the aqueous compositions of the invention, a titanium phosphate colloid adheres thereto, which serves to accelerate the formation of a zinc phosphate conversion coating by providing crystal nuclei around which the zinc phosphate coating can form. The resulting zinc phosphate coating has excellent characteristics as a base for siccative coatings such as paint. When the titanium compound concentration is lower than the amount specified, the colloid which becomes the crystal nuclei for the zinc phosphate coating is formed in too small a quantity. When the titanium compound concentration is higher than the amount specified, no enhanced effect is obtained. The phosphate and/or acid phosphate concentration specified is also present for the same purpose, i.e. to provide an adequate quantity of titanium phosphate colloid on the ferrous metal surface.

The pyrophosphate has the beneficial effect of micronizing the zinc phosphate conversion coating. When the concentration of pyrophosphate is below the range specified, adequate micronizing is not achieved. When its concentration is above the range specified, the pyrophosphate tends to react with the iron in the ferrous metal surface, resulting in the inhibition of formation of a zinc phosphate conversion coating.

When the carbonate and/or acid carbonate is employed in a quantity lower than that specified, the pH buffer effect is not obtained, i.e. when the pH of the present aqueous pretreatment composition is lower than the required values, the pyrophosphate ion tends to react with the ferrous metal surface, resulting in the inhibition of the subsequent zinc phosphate conversion coating formation. On the other hand, too high a pH value does not give a preferred conversion coating for pretreatments of electro coating.

When the present aqueous surface preparation compositions are used in the pretreatment of ferrous metal surfaces, such compositions can be used for long periods of time, and provide a base for uniform, dense zinc phosphate conversion coatings. The surface preparation compositions of the present invention are especially effective for preparing ferrous metal surfaces for zinc phosphate treatment for electro coating. The long-term stability of the instant surface preparation compositions is particularly advantageous in the dipping type treatment of metals in which a large quantity of surface preparation composition is employed.

The invention is illustrated by the following Examples, in which the term "%" refers to percent by weight.

EXAMPLE I

An aqueous surface treatment composition was prepared using the following quantities of ingredients:

titanium sulphate	5%
anhydrous secondary sodium phosphate	55%
anhydrous sodium pyrophosphate	15%
water	15%
sodium bicarbonate	10%

The above ingredients, except for the sodium bicarbonate, were heated at a temperature maintained in the range of 100° to 120°C with stirring until the water content was reduced to 1.5% or lower (about 2 hours). To the powder so obtained, the sodium bicarbonate was added and evenly mixed together.

The above solid mixture was then diluted with sufficient water to give a solution having a concentration of 0.07% of the mixture.

EXAMPLE II

An aqueous surface treatment composition was prepared using the following quantities of ingredients:

titanium sulphate	10%
anhydrous secondary sodium phosphate	45%
anhydrous sodium pyrophosphate	15%
water	10%
sodium bicarbonate	20%

A solid mixture was formed in accordance with the process of EXAMPLE I, and the mixture was added to sufficient water to give a solution of 0.1% concentration.

EXAMPLE III

An aqueous surface treatment composition was prepared from the following ingredients using the procedure of EXAMPLE I, except that the solid mixture formed was diluted with water to form a 0.05% aqueous solution:

titanium sulphate	5%
anhydrous secondary sodium phosphate	55%
anhydrous sodium pyrophosphate	15%
water	10%
sodium bicarbonate	10%
sodium carbonate	5%

EXAMPLE IV

Each of three degreased commercial cold rolled steel plates was treated with one of the new aqueous compositions of EXAMPLES I, II and III, i.e. one plate was treated with the composition of EXAMPLE I, a second plate with the composition of EXAMPLE II, etc. The plates were treated by dipping them for 1 minute in the aqueous composition, allowing excess liquid to drip off, and immediately dipping them into a zinc phosphate conversion coating bath (Nippon Paint Co. "GRANODINE SD 2000") for 2 minutes at a bath temperature of 50°C. The plates were then washed with water, dried, and evaluated; in addition, the above procedure was repeated with an additional three steel plates after the aqueous compositions of EXAMPLES I, II and III had stood for 10 days. The results obtained are given in the Table below EXAMPLE VIII, together with the pH values of the pretreatment compositions.

The following Examples are given for comparison purposes, using aqueous surface treatment compositions in accordance with the teachings of the prior art.

EXAMPLE V

An aqueous surface treatment composition was prepared from the following ingredients:

titanium sulphate	5%
anhydrous secondary sodium phosphate	55%
anhydrous sodium pyrophosphate	15%
water	25%

A solid mixture was formed from the above ingredients in accordance with the procedure of EXAMPLE I (except that all of the above ingredients were mixed together and heated to form the solid mixture). A 0.05% aqueous solution was formed according to the procedure of EXAMPLE I.

EXAMPLE VI

An aqueous surface treatment composition was prepared from the following ingredients in accordance with the procedure of EXAMPLE V except that the solid mixture was diluted with water to form a 0.1% aqueous solution.

titanium sulphate	5%
anhydrous secondary sodium phosphate	60%
anhydrous sodium pyrophosphate	15%
water	18%
sodium hydroxide	2%

EXAMPLE VII

An aqueous surface treatment composition was prepared from the following ingredients in accordance with the procedure of EXAMPLE V except that the solid mixture was diluted with water to form a 0.07% aqueous solution.

titanium sulphate	10%
anhydrous secondary sodium phosphate	70%
water	18%
sodium hydroxide	2%

EXAMPLE VIII

Six degreased commercial cold rolled steel plates of the type used in EXAMPLE IV were treated according to the procedure of EXAMPLE IV. The results obtained are given in the Table below for comparison purposes.

TABLE

Surface Treatment Composition Example No.	Immediately following preparation of surface treatment composition		10 days after preparation of surface treatment composition	
	Appearance of Steel surface*	pH of surface treatment composition	Appearance of Steel surface*	pH of surface treatment composition
I	O	9.0	O	9.0
II	O	8.7	O	8.7
III	O	9.0	O	9.0
V	O	8.7	X	8.1
VI	O	9.0	Δ	8.8
VII	Δ	8.5	X	7.8

* Following the zinc phosphate conversion coating treatment.

Evaluation criteria used in the above Table for the appearance of treated surfaces:

O : Formation of uniform and dense zinc phosphate coating.

Δ : Unevenness in zinc phosphate coating.

X : Yellow rust; tempering observed.

CLAIMS

1. An aqueous solution for the treatment of ferrous metal surfaces, which solution comprises:
   - (a) titanium compound in amount from 1 to 100 parts per million by weight, measured as titanium;
   - (b) phosphate and/or acid phosphate in amount totalling from 50 to 1500 parts per million by weight, measured as PO_4;
   - (c) pyrophosphate in amount from 10 to 300 parts per million by weight, measured as P_2O_7; and
   - (d) carbonate and/or acid carbonate in amount totalling 20 to 1500 parts per million by weight, measured as CO_3;

   the solution having a pH from 8.5 to 9.5.
2. A solution according to claim 1 wherein the titanium compound is either titanium sulphate or titanium oxide.
3. A solution according to claim 1 or 2 wherein (b), (c) and (d) are each present in the form of an ammonium or an alkali metal salt.
4. A solution according to any one of the preceding claims which contains a rust-inhibiting quantity of nitrite ion.
5. A process for pretreating a clean ferrous metal surface, which process comprises applying to the surface a solution claimed in any one of the preceding claims.

6. A process according to claim 5 wherein the ferrous metal surface is immersed in the aqueous composition.

7. A process according to claim 5 or 6 wherein the ferrous metal surface is subsequently treated with a zinc phosphate conversion coating composition.

8. A solid composition comprising:
  (a) titanium compound in amount from 1 to 100 parts by weight, measured as titanium;
  (b) phosphate and/or acid phosphate in amount totalling from 50 to 1500 parts by weight, measured as PO_4;
  (c) pyrophosphate in amount from 10 to 300 parts by weight, measured as P_2O_7; and
  (d) carbonate and/or acid carbonate in amount totalling 20 to 1500 parts by weight, measured as CO_3.

9. A composition according to claim 8 wherein the titanium compound is either titanium sulphate or titanium oxide.

10. A composition according to claim 8 or 9 wherein (b), (c) and (d) are each present in the form of an ammonium or an alkali metal salt.

11. A composition according to any one of claims 8 to 10 which contains a rust-inhibiting quantity of nitrite ion.

12. A process for the preparation of a composition claimed in any one of claims 8 to 11, which process comprises:
  (A) mixing together in water (a), (b) and (c) as defined in claim 8;

(B) heating the aqueous mixture to remove substantially all of the water therein; and

(C) mixing the resulting solid residue with (d) as defined in claim 8.

13. A process according to claim 12 wherein step (B) is carried out at a temperature of 100° to 120°C.