Patented Apr. 4, 1950 2,502,441

UNITED STATES PATENT OFFICE

2,502,441

PHOSPHATE COATING OF METALS

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No Drawing. Application November 22, 1946, Serial No. 711,810

15 Claims. (Cl. 148—6.15)

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The present invention relates to improvements in a composition and a process for depositing phosphate coating on metal surfaces when employed in phosphate coating solutions, and more particularly to compositions which will not only accelerate the deposition of a phosphate coating upon the surface of metals such as ferrous metals and other metals such as aluminum, zinc, magnesium and ternplate, but also condition the coating obtained by improving the quality thereof.

It is therefore an object of the invention to provide a composition which, when added to a phosphate coating solution, will cause accelerated deposition of phosphate coatings on ferrous and other metal objects treated with such solution.

It is another object to provide a composition which will, when added to phosphate coating solutions, promote uniformity, hardness, and adherence of phosphate coatings obtained when treating metal objects with such solution.

It is a further object to provide an improved method of producing phosphate coatings on metal articles employing the novel phosphate coating solutions.

A proposal has already been made in German Patent No. 584,411 to add water soluble molybdenum compounds to phosphating baths in order to provide accelerated deposition of a coating containing a mixture of phosphates and molybdenum oxides. However, it has been found that coatings produced from such baths containing a molybdenum compound tend to have poor adherence to the metal surface and have an undesirable soft or "spongy" nature rendering them inefficient as rust retarders and of poor quality in forming a strong bond with paint, enamel and other organic finishes.

In accordance with the present invention, it has been found that consistently uniform, adherent and hard phosphate coatings, which also have excellent corrosion resistant and paint bonding properties, may be obtained if the phosphating solution is employed to which a small quantity of a water soluble molybdenum or tungsten compound such as the molybdic and tungstic acid compounds, molybdic acid, tungstic acid, their anhydrides, and their water soluble salts, and a small quantity of a phenolic substance, such as, for example, the tannins, tannin nuclei, and tannin derivatives have been added.

The addition of such molybdenum or tungsten compound in combination with a phenolic compound not only accelerates and promotes the

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production of a phosphate coating, but also produces desirable effects in the quality and consistency of the coating obtained.

It has also been found that phosphate coating solutions, in which the major ingredient is a primary phosphate of the alkali group, that is, the primary alkali metal or ammonium phosphates, will give good phosphate coatings when they contain a small quantity of the novel accelerating combination in accordance with the invention. In the absence of such accelerating combination little or no phosphate coating is obtained from solutions containing such phosphates.

In addition, the use of the accelerating combination in accordance with the invention renders it possible to reduce the amount of free phosphoric acid usually present in solutions of which the major constituent is a monobasic phosphate of a heavy metal, such as zinc, manganese, or iron. In other words, phosphate coating solutions may be employed in accordance with the invention at a higher pH than in usual practice, namely, at a pH of about 3.2 to about 5.5 instead of at about 2.5.

Molybdenum compounds are preferably employed in accordance with the invention, but tungsten compounds possess similar properties. The following compounds are, for example, suitable: ammonium, sodium, potassium, molybdates and tungstates, and molybdic and tungstic acids and acid anhydrides. The quantity of molybdenum or tungsten compounds employed in a phosphate coating composition in accordance with the invention may range from 0.1% to 10% of the quantity of solid acid phosphate salt present. Preferably, the quantity of such compounds used is between 0.5% and 2.0% as higher concentrations tend toward the production of softer coatings.

The phenolic ingredients of the novel composition in accordance with the invention are preferably tannins, phenolic tannin derivatives and related phenolics. However, other phenols, such as phenol itself, possess the desirable effect in the combination in accordance with the invention but in some instances to a considerably lesser degree. Examples of suitable tannins are as follows: quebracho, cutch, sumac, chestnut, nut galls, spruce, fustic, and quercitron. Quebracho is the preferred material. Examples of other suitable phenolics are as follows: phenol, catechol, resorcinol, hydroquinone, pyrogallol, pyrogallic acid, gallic acid, phloroglucinol and the like. The polyhydric phenolic com-

pounds, catechol, pyrogallol, pyrogallic acid, gallic acid and resorcinol are preferred.

The quantity of phenol compound to be used in combination with the molybdenum or tungsten compound in accordance with the invention may vary between 0.1% and 10% preferably between 0.5% and 2% of the solid acid phosphate salt.

It has been found preferable to use the phenolic compounds in amounts approximately equal to the quantity of molybdenum or tungsten compound used. However, the proportion may be varied within the limits of the quantities given above.

The phenolic compounds and molybdenum or tungsten compounds may be added separately or together to a phosphate coating solution or may be incorporated in a solid phosphating composition before preparation of the aqueous phosphate coating solution.

It is desirable to incorporate wetting or cleaning agents, which are effective in acid solution, to phosphate coating solutions prepared in accordance with the invention, but such wetting or cleaning agents may be omitted if the metal articles to be coated have been thoroughly cleaned before treatment with the solution.

The following wetting and cleaning agents are, for example, suitable for use in phosphate coating compositions prepared in accordance with the invention:

Sulphonated fatty alcohols.
Alkylated aromatic sulphonates.
Complex sulphonated amides.
Polyhydric alcohol anhydride ethers esterified with fatty acids such as sorbitan monolaurate.
Non-ionic wetting agents such as polyethylene oxide derivatives of fatty alcohols or acids, or of other substances containing hydroxyl or carboxyl groups.

Any of these are suitable for use as the wetting and cleaning agents which are recited in the examples given below, which will serve to illustrate the invention.

Example 1

A phosphate solution is prepared containing approximately 2 ounces per gallon of a composition of the following formula:

	Per cent
NaH_2PO_4	90.0
MoO_3	1.0
Quebracho	0.5
Wetting and cleaning agent	8.5

This solution when used hot and applied for two minutes by pressure spraying to a ferrous metal surface will convert the surface into a prosphate coating averaging about 100 milligrams in weight per square foot of surface.

If the MoO_3 and quebracho are omitted from the same type of acid phosphate solution, consistent deposition of a coating is difficult to accomplish. Results are erratic; the coating being non-uniform, meagre, or completely non-existent.

If the molybdenum compound without the tannin is used in the same type of solution, a deposit results which seems amorphous in structure, is non-adherent to the surface, and of no value as a foundation for painting.

If the tannin is used without the molybdenum compound in such solution, deposition of a coating seems to be completely inhibited.

Example 2

An aqueous solution is prepared containing about 2 ounces per gallon of the following composition:

	Per cent
$NH_4H_2PO_4$	90.0
MoO_3	1.0
Sumac tannin	1.0
Wetting and cleaning agents	8.0

This solution gives results similar to those obtained in Example 1 when used in the same manner.

Example 3

A phosphating bath is prepared containing about 2 ounces per gallon of the following composition:

	Per cent
NaH_2PO_4	90.5
H_3PO_4 (75%)	4.5
Ammonium molybdate	1.0
Catechol	1.0
Wetting and cleaning agents	3.0

Immersion of a steel article in such bath for 4 minutes at a temperature of 160° F. produces about 100 milligrams of a hard continuous coating per square foot of surface.

Example 4

A phosphating bath is prepared containing about 2 ounces per gallon of the following composition:

	Per cent
$ZnH_4(PO_4)_2$	50.5
H_3PO_4(75%)	47.5
MoO_3	1.0
Quebracho	1.0

A steel panel immersed in such bath for 4 minutes at 160° F. will receive a hard coating weighing about 150 milligrams per square foot.

Example 5

A phosphating solution containing 3 ounces per gallon of the following composition is prepared:

	Per cent
NaH_2PO_4	91.9
H_3PO_4	4.5
$Na_2WO_4.2H_2O$	.6
Quebracho	1.0
Wetting and cleaning agents	3.0

This phosphating solution will produce about 85 milligrams of a hard, continuous, iridescent coating per square foot when used in the same manner as the solution in Example 3.

Example 6

A phosphating solution containing 3 ounces per gallon of the following composition is prepared:

	Per cent
NaH_2PO_4	90.5
H_3PO_4(75%)	4.5
Ammonium molybdate	1.0
Resorcinol	1.0
Wetting and cleaning agents	3.0

This solution will produce results similar to those described in Example 3.

While the compositions given in the above examples in most instances include wetting and cleaning agents, they may be omitted and equal results will be obtained if the metal articles are thoroughly cleaned before treatment.

Also, while the phosphate coating solutions may be used in accordance with the invention at a pH between 3.2 and 5.5, it has been found preferable to adjust the pH value thereof to between 3.2 and 3.8 when the coating is obtained by tank immersion and to adjust the pH value thereof to 4.8 to 5.2 when a spray machine is used to apply the solution to the articles being coated.

We claim:

1. A phosphating composition comprising an acid salt of phosphoric acid and a water soluble compound selected from the group consisting of molybdic acid compounds and tungstic acid compounds and a phenol, said latter two ingredients each being present in a quantity ranging from 0.1% to 10% of the quantity of acid salt of phosphoric acid.

2. A phosphating composition comprising an acid salt of phosphoric acid and a water soluble compound selected from the group consisting of molybdic acid compounds and tungstic acid compounds and a phenol, said latter two ingredients each being present in a quantity ranging from 0.5% to 2% of the quantity of acid salt of phosphoric acid.

3. A phosphating composition comprising an acid salt of phosphoric acid, a water soluble compound selected from the group consisting of molybdic acid compounds and tungstic acid compounds, and a polyhydric phenol, said latter two ingredients each being present in a quantity ranging from 0.1% to 10% of the quantity of acid salt of phosphoric acid.

4. A phosphating composition comprising an acid salt of phosphoric acid, a water soluble compound selected from the group consisting of molybdic acid compounds and tungstic acid compounds, and a tannin containing at least one free phenolic hydroxy group, said latter two ingredients each being present in a quantity ranging from 0.1% to 10% of the quantity of acid salt of phosphoric acid.

5. A phosphating composition comprising an acid salt of phosphoric acid, a water soluble compound selected from the group consisting of molybdic acid compounds and tungstic acid compounds, and quebracho, said latter two ingredients each being present in a quantity ranging from 0.1% to 10% of the quantity of acid salt of phosphoric acid.

6. A phosphating composition comprising an acid salt of phosphoric acid, a water soluble molybdic acid compound and a phenol, said latter two ingredients each being present in a quantity ranging from 0.1% to 10% of the quantity of acid salt of phosphoric acid.

7. A phosphating composition comprising an acid salt of phosphoric acid, a water soluble molybdic acid compound and a polyhydric phenol, said latter two ingredients each being present in a quantity ranging from 0.1% to 10% of the quantity of acid salt of phosphoric acid.

8. A phosphating composition comprising an acid salt of phosphoric acid, a water soluble molybdic acid compound and a gallic acid, said latter two ingredients each being present in a quantity ranging from 0.1% to 10% of the quantity of acid salt of phosphoric acid.

9. A phosphating composition comprising an acid salt of phosphoric acid, a water soluble molybdic acid compound and a tannin containing at least one free phenolic group, said latter two ingredients each being present in a quantity ranging from 0.1% to 10% of the quantity of acid salt of phosphoric acid.

10. A phosphating composition comprising an acid salt of phosphoric acid, a water soluble molybdic acid compound and quebracho, said latter two ingredients each being present in a quantity ranging from 0.1% to 10% of the quantity of acid salt of phosphoric acid.

11. A phosphating composition comprising an acid salt of phosphoric acid, a water soluble molybdic acid compound and catechol, said latter two ingredients each being present in a quantity ranging from 0.1% to 10% of the quantity of acid salt of phosphoric acid.

12. A phosphating composition comprising an acid salt of phosphoric acid, a water soluble compound selected from the group consisting of molybdic acid compounds and tungstic acid compounds, and a phenol, said latter two ingredients being present in substantially equal quantities, the quantity of each ranging from 0.1% to 10% of the quantity of acid salt of phosphoric acid.

13. A phosphating composition comprising a primary phosphate of the alkali group and a water soluble compound selected from the group consisting of molybdic acid compounds and tungstic acid compounds and a phenol, said latter two ingredients each being present in a quantity ranging from 0.1% to 10% of the quantity of a primary phosphate of the alkali group.

14. A phosphating composition comprising a primary phosphate of the alkali group, a water soluble molybdic acid compound and quebracho, said latter two ingredients each being present in a quantity ranging from 0.2% to 5% of the primary phosphate of the alkali group.

15. A process of coating metal surfaces which comprises contacting the metal surfaces with an aqueous solution of an acid salt of phosphoric acid containing a water soluble compound selected from the group consisting of molybdic acid compounds and tungstic acid compounds and a phenol, said latter two ingredients each being present in a quantity ranging from 0.1% to 10% of the quantity of the acid salt of phosphoric acid.

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