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[54] **METHOD AND COMPOSITION FOR PHOSPHATIZING STEEL UNDER PRESSURE**

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[58] **Field of Search** ..... 148/6.15 R, 6.15 Z

[56] **References Cited**

UNITED STATES PATENTS

1,303,627	5/1919	Baines	148/6.15 R
2,516,139	7/1950	Mazia	148/6.15 R
2,826,517	3/1958	Miller	148/6.15 Z
3,116,178	12/1963	Upham	148/6.15 Z

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[57] **ABSTRACT**

The heat and corrosion resistance of manganese phosphate coatings on ferrous surfaces can be greatly improved by modifying a conventional phosphatizing solution to reduce the ferrous ion content thereof, adding a given quantity thereto of the manganese salt obtained from an acid selected from the group consisting of citric, tartaric, gluconic, and saccharic acids and then carrying out the coating process in a closed chamber under a steam pressure in excess of one pound per square inch.

9 Claims, No Drawings

METHOD AND COMPOSITION FOR PHOSPHATIZING STEEL UNDER PRESSURE

This invention relates to the formation of phosphate coatings on ferrous surfaces and is more particularly directed to producing such coatings in a manner which will provide an unusual degree of resistance to heat and corrosion.

Ferrous surfaces can be satisfactorily protected against corrosion under most conditions by any one of several well-known phosphatizing treatments which form a relatively porous and insoluble coating capable of serving as a base for the application of such supplementary coatings as paints, lubricating oils, and preservative compounds. This type of combined coating has been found to be particularly useful for those military weapon components wherein the exterior surfaces thereof must display a relatively low reflectivity to light and moderate resistance to wear. While the elimination of the supplementary coating would obviously provide a highly desirable reduction in the time and cost required to process these military components, current phosphatizing techniques do not provide coatings with sufficient corrosion resistance to withstand the exceptionally severe conditions under which the weapons are frequently operated. For example, the ordinary manganese phosphate coating currently utilized to protect the surfaces of ferrous gun parts will generally provide no more than 8 hours of protection against the standard salt spray test required for military acceptance. Moreover, where the operation of the gun subjects the coated surfaces thereof to temperatures in excess of 275°F, the corrosion resistance thereof under the same salt spray test is drastically reduced, often to less than one hour of exposure.

Accordingly, it is an object of this invention to provide an improved method for treating ferrous surfaces to form a metal phosphate coating thereon with an unusual degree of resistance to heat and corrosion.

It is a further object of this invention to provide an immersion type of phosphatizing treatment for ferrous surfaces which can be readily performed under steam pressure in a closed and heated chamber.

Another object of the present invention resides in the provision of a manganese phosphate coating for ferrous surfaces which will eliminate the need for any supplementary coating of the type currently utilized to furnish the relatively low reflectivity to light and the moderate resistance to wear required of many of the component parts of military weapons.

Still another object of this invention is to provide an improved phosphatizing composition for treating ferrous surfaces to form a relatively complex combination of manganese and iron phosphates which produce a tenacious coating characterized by a lesser porosity and a far greater resistance to heat and corrosion than similar coatings in current use.

It has been found that the foregoing objects can best be accomplished by providing a phosphatizing bath in which the amount of iron therein does not exceed 1 percent and which also includes a controlled quantity of the salt formed by reacting manganese or the compounds thereof with a polyhydroxy acid selected from the alpha-hydroxy or carboxylic groups containing 4 to 6 carbon atoms with the particular atom adjacent to at least one of the carboxyl groups being replaced by a hydroxyl group acid. In addition, the phosphatizing treatment is carried out in a closed chamber under a steam pressure in excess of one (1) psig.

It is well known that an insoluble coating of manganese phosphate can be formed on a ferrous surface by any one of several commercial aqueous solutions which contain a mixture of dihydrogen phosphates of manganese and iron and a quantity of free phosphoric acid. These compositions react with the ferrous surface to produce a relatively porous, crystalline coating which must be additionally treated with a preservative compound to provide up to 24 hours of protection against the corrosive effects of the standard 5% salt spray tests set forth in ASTM procedure B117–61. Such protection, however, is not adequate for those military components which will be subjected to the severe corrosive conditions encountered in a humid or marine environment. Moreover, where the coated components also involve temperatures in excess of 275°F, the degree of protection against corrosion is appreciably reduced, often to less than one hour.

In accordance with the present invention, however, investigation has shown that the porosity of the coatings formed with conventional phosphatizing treatments can be considerably reduced by carrying out the process in an autoclave under steam pressure. Since an increase in the steam pressure provides a corresponding increase in temperature, the formation of the phosphate coating proceeds at a faster rate and consequently provides a finer and less porous structure than would be the case under atmospheric pressure. It is well known that the greater the porosity of the coating, the greater the proportion of the surface area which will be exposed to corrosive deterioration. While a steam pressure of 1 psig provides satisfactory results, a higher pressure will reduce the time required to form a given thickness of phosphate coating. This is a highly desirable relationship, not only for the sake of economy but because the required chemical activity of some of the organic salts of manganese is much slower than others as will be shown in the examples to be described hereinafter.

Further experimentation has indicated that a desirable reduction in the porosity of a manganese phosphate coating on a ferrous surface is considerably enhanced whenever the initial quantity of the ferrous iron in the phosphatizing solution is held to a minimum. While most commerical solutions average about 3 percent by weight of iron, indications are that the corrosion resistance of the resulting phosphate coatings increases in inverse ratio to the proportion of the ferrous phosphate incorporated therein. Consequently, while a certain proportion of ferrous phosphate is required to produce the necessary crystalline structure of the coating, it has been found that the phosphatizing solution should contain between 0.01–1.0 percent of ferrous iron preferably within the lower half of such range.

Furthermore, during the formation of the manganese phosphate coating it is essential that the amount of iron etched from the ferrous surface to be coated also be held to a minimum. It has been found that such etching of the iron can be considerably reduced by the addition to the phosphatizing solution of a given quantity of the manganese salt produced by the reaction between the metal or a compound thereof and a polyhydroxy carboxylic acid. For the purpose of this invention, the acid is preferably selected from the carboxylic group containing 4 to 6 carbon atoms with the particular carbon

atom adjacent to at least one of the carboxyl groups being replaced by a hydroxyl group. Examples of acids falling within this classification are citric, tartaric, gluconic, and saccharic with the chelation tendencies thereof decreasing in the particular order in which the acids are named. For some reason not yet fully understood, the presence of these manganese saltS in a conventional phosphatizing solution modified by a reduction in the ferrous iron content thereof actually inhibits the extent to which iron will be etched from the ferrous surface being coated during the formation of such coating. As a result, the ferrous phosphate portion of the complex coating is considerably reduced over that of present commerical types of phosphate coatings and consequently produces a finer and less porous structure which is better able to resist the combined effects of heat and corrosion.

To form the phosphatizing solution or bath of the present invention, manganese dihydrogen phosphate, manganese carbonate, ferrous dihydrogen phosphate and phosphoric acid are placed in aqueous solution in quantities which will provide the following ingredients expressed in percentage by weight:

Constituents	Percentage
Manganese	0.1–3.0
Phosphate	0.2–4.0
Iron	0.01–1.0

The composition of the bath is formulated within these ranges to provide a total acid content of from 15 to 75 points, a point being defined as the number of milliliters of 1/10 normal sodium hydroxide required to titrate a 10 milliliter sample of the bath to a phenolphthalein end point. At the same time, the bath is also adjusted to yield a free acid content of 1 to 5 points thereby providing a total acid to free acid ratio of between 5 to 1 and 15 to 1. A limiting factor in these adjustments is the necessity for maintaining a pH in excess of 2.0, preferably between 2.1 and 3.1. The percentages of both the manganese and the iron are preferably limited to the lower portions of the given ranges.

The bath is completed by adding from 10 to 15 grams per liter of one of the aforementioned manganese salts in such quantity that the desired acid ratio will be maintained without causing the total manganese content of the solution to exceed 5.0 percent by weight. Where optimum corrosion resistance is desired, the bath is formulated to include the citrate salt of manganese. However, while those baths which contain the tartrate and gluconate salts of manganese are operative at temperatures only slightly above that at which steam will be formed (212°F) thereby permitting the pressure in the autoclave to be held as low as 1 psig, the selection of manganese citrate requires an operating temperature of at least 260°F. In order to provide such increase in temperature, the pressure of the steam within the autoclave must be raised to about 22 psig. Thus, where economy of the coating process is a dominant factor, the tartrate and gluconate salts of manganese are preferred.

Examples I through III are illustrative of the limits to which the phosphatizing bath must be adjusted to provide optimum conditions for coating a ferrous surface to provide an unusual degree of resistance to corrosion when subjected to ASTM procedure B117–61 salt spray corrosion test, even after the coating had previously been heated to a temperature as high as 450°F.

Example I

A manganese phosphatizing bath was prepared to provide an aqueous solution formulated to provide:

Free Acid (FA)	4.2 points
Total Acid (TA)	31.9 points
Ratio of total Acid to Free Acid (TA/FA)	7.6 to 1
Iron	0.19% by weight
pH	2.1

To each liter of this solution was added 14 grams of manganese citrate. The resulting bath was then placed in an autoclave containing the steel specimens to be coated and then heated for a total of 43 minutes to provide a steam pressure of 22 psig which was maintained for 15 minutes. The coated specimens were removed from the autoclave and separated into two groups. Those in the first group were tested for their resistance to salt spray corrosion in accordance with the method described in ASTM procedure B117–61 for a total of 500 hours of continuous exposure without any appearance of rust. The specimens in the second group were rinsed, dried, and then heated in an oven for one hour at a temperature of 450°F. When subjected to the same salt spray testing as used for the unheated specimens, the heated specimens showed no indication of rusting after 180 hours of exposure.

Example II

A manganese phosphatizing bath was prepared in accordance with the following formulation:

Free Acid (FA)	2.9 points
Total Acid (TA)	14.9 points
Ratio of Total Acid to Free Acid (TA/FA)	5.1 to 1
Iron	0.05% by weight
pH	3.1

The bath was modified by adding 10 grams of manganese tartrate for each liter of solution present and then placed in an autoclave containing the steel specimens to be coated. During a processing period of 30 minutes, the autoclave was heated to provide a steam pressure therein of 1 psig which was maintained for 15 minutes. After removal from the autoclave, some of the specimens were tested for their resistance to the corrosive effects of the type of salt spray atmosphere specified in ASTM procedure B117–61. No rust was found after a total of 720 hours of continuous exposure. The remaining specimens were rinsed, dried, and then heated in an oven for one hour to a temperature of 450°F. These specimens withstood the same duration of salt spray testing as the unheated specimens without evidence of rusting.

EXAMPLE III

A manganese phosphatizing bath was prepared in accordance with the following formulation:

Free Acid (FA)	1.6 points
Total Acid (TA)	13.1 points
Ratio of Total Acid to Free Acid (TA/FA)	8.2 to 1
Iron	0.05% by weight
pH	2.9

This formulation was thereafter modified by adding thereto 10 grams of manganese gluconate per liter of solution and placed in an autoclave. The latter was then heated for a total of 43 minutes during which 1 psig of

steam pressure was maintained for a period of 15 minutes. Thereafter, several of the specimens were subjected to a salt spray corrosion atmosphere of the type specified in ASTM procedure B117–61 for a total of 720 hours of exposure without any signs of rusting. The remaining specimens were rinsed, dried, and heated in an oven for one hour at 450°F and then subjected to the same salt spray testing as the unheated specimens for 380 hours of exposure without any evidence of rusting.

Although none of the foregoing examples were tested to the point of actual rusting, it should be pointed out that manganese phosphate coatings produced in accordance with this invention are fully capable of withstanding more than 1000 hours of exposure to a corrosive salt spray atmosphere even when subjected to temperatures as high as 450°F. This is a phenomenal improvement over the corresponding 1½ to 2 hours of protection afforded by comparable coatings produced with commercial phosphatizing baths. Moreover, the coating produced in accordance with this invention provides the non-reflective surface and moderate wear resistance required of military weapon components. Furthermore, the greater density of the coating over comparable commercial coatings permits a significant decrease in the thickness required to provide a given corrosion resistance. As a result, the processing of the present invention may be accomplished more rapidly and therefore more economically.

While the various formulations of the phosphatizing bath and the processing techniques are limited to certain preferred relationships, it will also be obvious to persons skilled in the art that various modifications to the examples and details described herein are possible without departing from the spirit and the scope of the present invention. Therefore, it is desired that the present invention shall not be limited except insofar as it is made necessary by the prior art and by the spirit of the appended claims.

We claim:

1. A method for treating ferrous surfaces to form a manganese phosphate coating thereon characterized by the ability to withstand the corrosive effect of a 5% salt spray test for more than 750 hours, said method comprising the steps of,

formulating a manganese phosphatizing bath containing from 0.01 to 1.0 percent of ferrous iron,

adding from 0.1 to 2.0 percent by weight of the manganese salt of a carboxylic acid selected from the group containing 4 to 6 carbon atoms with the particular carbon atom adjacent to at least one of the carboxyl groups being replaced by a hydroxyl group, said salt being added without exceeding a total of 5.0% manganese in said bath, and

subjecting said bath and the ferrous surfaces to be coated to a steam pressure in excess of atmospheric pressure for a period of from 1 to 60 minutes selected in inverse ratio to the particular steam pressure being utilized.

2. A method for treating ferrous surfaces to form a manganese phosphate coating thereon characterized by the ability to withstand, subsequent to being heated to a temperature as high as 450°F, the corrosive effect of a 5% salt spray test for more than 750 hours, said method comprising the steps of,

formulating a manganese phosphatizing bath wherein the ratio of total acid to free acid is between 5 to 1 and 15 to 1 and the pH ratio is in excess of 2.0,

adding from 0.1 to 2.0 percent by weight of the salt obtained by reacting manganese with an organic acid selected from the carboxylic group containing 4 to 6 carbon atoms with the particular carbon atom adjacent to at least one of the carboxyl groups being replaced by a hydroxyl group, the amount of said added manganese salt being selected to maintain said acid ratio and said pH without causing the total manganese content of said bath to exceed 5.0 percent,

confining said bath and the ferrous surfaces to be coated within a sealed container, and

heating the interior of said container to provide a steam pressure of between 1 and 22 psig for at least 15 minutes.

3. A method for treating ferrous surfaces to form a manganese phosphate coating thereon adapted to resist the corrosive effect of a standard 5% salt spray test comprising the steps of,

formulating an aqueous manganese phosphatizing bath to include between 0.01 and 1.0 percent of ferrous iron,

enriching the bath with from 0.1 to 2.0 percent by weight of the manganese salt of a carboxylic acid selected from the group consisting of citric, tartaric, gluconic, and saccharic acids,

confining the bath and the ferrous surfaces to be coated thereby within an autoclave, and

subjecting the contents to steam pressure in excess of one psig for at least 15 minutes during the formation of the phosphate coating on the ferrous surfaces.

4. An aqueous bath for coating ferrous parts with a low porosity, non-reflective metal phosphate surface, said bath consisting essentially of,

a mixture of manganese and ferrous dihydrogen phosphates providing from 0.1 to 3.0 percent by weight of manganese and from 0.01 to 1.0 percent by weight of ferrous iron,

sufficient phosphoric acid to provide a total acid to free acid ratio of between 5 to 1 and 15 to 1 and a pH between 2.1 and 3.1, and

a manganese salt formed from a carboxylic acid selected from the group consisting of citric, tartaric, gluconic, and saccharic acids, said salt being added to the bath in a percentage by weight which will maintain the existing acid ratio and pH without increasing the total manganese content above 5.0 percent.

5. The phosphatizing bath defined in claim 4 wherein said salt is manganese citrate.

6. The phosphatizing bath defined in claim 4 wherein said salt is manganese tartrate.

7. The phosphatizing bath defined in claim 4 wherein said salt is manganese gluconate.

8. In an aqueous manganese base phosphatizing bath for coating ferrous parts with a low porosity, non-reflective metal phosphate surface,

a mixture of manganese and ferrous dihydrogen phosphates providing from 0.1 to 3.0 percent by weight of manganese and from 0.01 to 1.0 percent by weight of ferrous iron,

from 10 to 14 grams per liter of manganese citrate such that the total manganese content of the bath does not exceed 5.0 percent by weight, and

sufficient phosphoric acid to provide from 0.2 to 4.0 percent of phosphate while maintaining a total acid to free acid ratio of between 5 to 1 and 15 to 1 and a pH of between 2.1 and 3.1.

9. The phosphatizing bath defined in claim 8 including sufficient manganese carbonate to adjust the total acid to free acid ratio to about 7.5 to 1.

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