This invention relates to a rustproofing ferrous article and to a method of producing the same.

Numerous methods of rustproofing iron and steel objects have been proposed and used, and many of these compositions involved the use of phosphoric acid and chromates. These processes, however, all present difficulties in one respect or another, and particularly in that all of them require dipping of the iron or steel object in a bath, and also in that the iron or steel is attacked by the bath with the evolution of hydrogen.

By means of the present invention a much simplified method of producing a resistant coating upon iron and steel is provided, and at the same time the coating composition may be applied by spraying or brushing, and does not attack the metal. In connection with large and bulky articles such as automobile bodies, this elimination of the necessity for a bath is of extreme importance.

In accordance with this invention an aqueous solution of a soluble hexavalent chromium oxygen compound, preferably an alkali metal dichromate, and phosphoric acid is sprayed or brushed upon the ferrous object. The ratio of chromate to phosphoric acid, as well as the concentration of the solution must be adjusted within specific ranges, however, in order to prevent etching or solution of the ferrous metal object in the bath, and in order to produce a satisfactory coating.

The chromate may be supplied as chromic anhydride, chromate or dichromate. An alkali metal dichromate such as sodium dichromate is preferred, and should be present in an amount equivalent to at least 25% of the phosphoric acid present. The stability of the coating increases as the ratio of the dichromate increases from this point up to approximately one part for each part of phosphoric acid (H₃PO₄). A ratio of about 0.8 to 0.9 of sodium dichromate to one part of phosphoric acid is preferred from the standpoint of cost and stability.

The ratio of sodium dichromate to phosphoric acid may be increased indefinitely, but above 1 to 1 the stability of the coating shows no appreciable increase, and there is, of course, no economy in increasing the amount of sodium dichromate.

Where chromic anhydride, or chromic acid, is used, at least 33 parts of the anhydride to 100 parts of phosphoric acid are preferred in order to prevent etching of the ferrous metal object in the bath. The 33 parts of the chromic anhydride are equivalent to about 25 parts of dichromate. Inasmuch as dichromate contains only about 67% Cr₂O₃, about 33% chromate as chronic anhydride is equivalent to 16% Cr₂O₃ as sodium dichromate.

Where the chromate such as sodium chromate is used there is of course one excess molecule of sodium hydroxide present for each molecule of Cr₂O₃. This sodium hydroxide will react with the phosphoric acid present to produce mono-sodium phosphate and if more than about 120 parts of Na₂Cr₂O₇·4H₂O are used for 100 parts of phosphoric acid, the phosphoric acid will be completely transformed to the mono-sodium phosphate, so that no free phosphoric acid will be present. Because of this, sodium chromate cannot be used as an equivalent in a higher ratio than 0.75 when calculated on its sodium dichromate equivalency.

With dilute solutions of the mixture an irregular coating is produced which does not give thorough protection. It is therefore preferred to use strong solutions containing phosphoric acid of the order of 10 to 20%, and sodium dichromate of the order of 10 to 15%. It will, of course, be realized that the actual amount of sodium dichromate which may be introduced is limited by the solubility of the material.

With the more dilute solutions of phosphoric acids it is preferred to use a wetting agent, such as sulfonated higher alcohols such as lauryl, myristyl, and oleyl (known to the trade as “Gardinol”) which are very effective in preventing streaking or spotting in concentrations of about 0.1%. Other wetting agents such as condensation products of naphthalene beta sulfonic acid with alcohols of three or more carbon atoms (known to the trade as “Neaks”) are likewise effective, although they are more easily decomposed. The Gardinols are effective for at least 24 hours after their addition to the solution. The wetting agents are further advantageous in that it is not so essential to remove thoroughly all oil and grease spots from the metal to be treated.

The wetting agents may likewise be used with more concentrated solutions if desired.

The solutions may be applied by spraying, brushing or dipping. The ferrous metal object is not noticeably attacked by the solution when dipped into it, even though it is maintained in a bath for several hours at high temperature. Iron submerged in a solution at 100° C. for several days shows no loss in weight.

After the solution has been applied to the ferrous object it is dried to produce the rustproofing coating. The drying may be carried out at any desirable temperature, but preferably above 100°.
C., with the most desirable range being from 120° C. to 200° C. At 120° C. the coating will dry in about 1½ hours or less, while at 200° C. 15 minutes is normally sufficient. The actual chemical reaction occurring during the evaporation is not understood, but apparently the coating reacts slightly with the iron to produce a complex insoluble iron compound which produces the rustproofing action. When the drying has been carried out at lower temperature, that is from 120° C. to 160° C., the excess re-agent in the solution is not rendered fully insoluble and may be washed off, but leaves a true rustproof coating apparently combined with the metal surface. At high temperature, that is at about 200° C., a greater proportion of the composition is rendered insoluble and produces what may be considered a second coating, which apparently adheres to the true rustproof coating beneath it.

The portion of the dried material which can be removed by washing contains no appreciable amount of iron, and in all cases the treated material gains in weight whether dried at high or low temperature.

Where the drying has been at high temperature, the coating produced is slightly yellow in color, and is highly resistant to corrosion by oxygen, many corrosive chemicals, and also to most dilute acids. The coating is extremely resistant to the salt spray, is fairly resistant to abrasion, and metal objects so coated may be bent without forming cracks in the coating. There is no visible attack on the surface of the metal during the drying, although some iron apparently enters the coating, since the highly acid nature of the coating is somewhat neutralized in the drying operation.

When the drying has been carried out at lower temperature, the initial coating produced is also slightly yellow in color, but this yellow coating may be substantially all washed off to leave a metallic surface with just a shade of yellowishness, and in some instances practically in its original condition so far as color is concerned. Nevertheless the metal is rustproof apparently to the same extent as where the drying is carried out at a higher temperature.

Chromium salts in which the chromium is in the basic ion do not appear to give the same protection, or even to give a satisfactory coating. The present coating is distinctly different from other coatings produced by phosphoric acids and dichromate mixtures in which the metal is attacked by the solution, with consequent loss in weight.

The coating produced by brushing or spraying and drying at higher temperatures is sometimes streaked in appearance. This streaking has no effect upon the resistance of the coating, and where the metal is to be painted over does not affect it in any way. However, where a finished surface is desired, and a uniform, evenly covered surface is important, it has been discovered that such a surface may be produced by the introduction into the solution of an inert, colloidal substance such as bentonite, clay, colloidal silica, or litharge, in amounts from 1 to 5%.

The colloidal material does not interfere in any way with the reaction or with the baking, but after the heating step the surface appears to be covered with dust. This dusty layer may be brushed or wiped off readily, and the resulting surface is exactly like that without the colloidal agent except that there is no streaking.

The solution here disclosed may be used for dipping as well as for brushing or spraying, but a dipped article is much more streaked and irregular than the brushed or sprayed one.

A typical composition may be prepared by dissolving 20 parts by weight of sodium dichromate crystals (Na$_2$Cr$_2$O$_7$·2H$_2$O) in 30 parts of 75% phosphoric acid diluted with 100 parts of water, yielding a solution of the following composition:

<table>
<thead>
<tr>
<th>Per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$Cr$_2$O$_7$·2H$_2$O</td>
</tr>
<tr>
<td>H$_3$PO$_4$</td>
</tr>
<tr>
<td>H$_2$O</td>
</tr>
</tbody>
</table>

where bentonite is included the composition may be suitably made up by adding 37.5 parts of bentonite to the above mixture yielding a composition containing

<table>
<thead>
<tr>
<th>Per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$Cr$_2$O$_7$·2H$_2$O</td>
</tr>
<tr>
<td>H$_3$PO$_4$</td>
</tr>
<tr>
<td>H$_2$O</td>
</tr>
<tr>
<td>Bentonite</td>
</tr>
</tbody>
</table>

In using either of these mixtures it is first necessary to clean the metal surface free from rust or grease by some well known means such as sand blasting and washing with an alkaline cleaning agent. Either of the above compositions may then be applied by brushing, spraying, or dipping and the coated metal dried or baked for approximately one-half hour at a temperature of about 200° C. Steel plates coated in this manner showed no rusting at the end of 24 hours in a 1% salt spray at room temperature.

The solutions herein described may be used either cold or hot, inasmuch as the solutions do not attack metal even when hot, and the solutions do not deteriorate at any temperature up to boiling.

By adding a small amount of liquid sodium silicate to the rustproofing solution a stiff gel may be obtained, which may be applied to metal surfaces by rubbing it on with a cloth, followed by subsequent drying.

The term "chromate" as used in the claims hereof includes chromic acid and chromic anhydride.

This application is a continuation of my co-pending application Serial No. 721,637 filed April 20, 1934.

I realize that considerable variation is possible in the details of the construction herein shown, and I do not intend to limit myself thereto, except as pointed out in the following claims, in which it is my intention to claim all the novelty inherent in the device as broadly as is permitted by the state of art.

What I regard as new, and desire to secure by Letters Patent, is:

1. A ferrous metal object having on a surface thereof an integral coating having the composition resulting from treating the ferrous metal object with an aqueous solution containing 10 to 25% phosphoric acid and chromate in a ratio equivalent to at least .25% of sodium dichromate to one part phosphoric acid, and drying the coated article.

2. A metal object having on a surface thereof an integral coating having the composition resulting from treating the ferrous metal object with an aqueous solution containing 10 to 70% phosphoric acid and an alkali metal dichromate in a ratio of at least .25 part dichromate to one part phosphoric acid, and baking the coated article.

3. A ferrous metal object having on a surface...
thereof an integral coating having the composition resulting from treating the ferrous metal object with an aqueous solution containing 10 to 20% phosphoric acid and sodium dichromate in a ratio of .9 part dichromate to one part phosphoric acid, and baking the coated article at a temperature of 200° C. for half an hour.

4. A ferrous metal object having on a surface thereof an integral coating of uniform appearance having the composition resulting from treating the ferrous metal object with an aqueous solution containing 10 to 20% phosphoric acid and sodium dichromate in a ratio of .9 part dichromate to 1 part phosphoric acid, and 5 to 20% of bentonite, and baking the coated article at a temperature of 200° C. for half an hour.

5. A composition of matter for use in rust-proofing ferrous articles comprising a chromate and a phosphoric acid, in a ratio equivalent to at least 25 parts of sodium dichromate to 100 parts of phosphoric acid, and water in an amount to provide a concentration of 10 to 20% phosphoric acid.

6. A composition of matter for use in rust-proofing ferrous articles comprising an alkaline metal dichromate and phosphoric acid in a ratio of at least 25 parts of dichromate to 100 parts of phosphoric acid, and water in an amount to provide a concentration of 10 to 20% phosphoric acid.

7. A composition as set forth in claim 6, in which the dichromate is sodium dichromate.

8. A composition as set forth in claim 6, in which the ratio of dichromate to phosphoric acid is of the order of .8 to .9 parts of dichromate to one part of phosphoric acid.

9. A composition of matter for use in rust-proofing ferrous articles comprising a chromate and phosphoric acid in a ratio equivalent to at least 25 parts of sodium dichromate to 100 parts of phosphoric acid, water in an amount to provide a concentration of 10 to 20% phosphoric acid, and an inert colloidal dispersing agent.

10. A composition as set forth in claim 9, in which the colloidal agent is bentonite.

11. A composition as set forth in claim 9, in which the colloidal dispersing agent is 5 to 20% of bentonite.

12. The method of producing a resistant coating upon ferrous metal objects which comprises coating the object with an aqueous solution of a chromate and phosphoric acid, the ratio of the chromate to the phosphoric acid being equivalent to at least 25 parts of sodium dichromate to 100 parts of phosphoric acid, without etching or partially dissolving the surface of said object, and drying the coated object.

13. The method of producing a resistant coating upon ferrous metal objects which comprises coating the object with an aqueous solution of an alkaline metal dichromate and phosphoric acid, the ratio of the dichromate to the phosphoric acid being at least 25 parts of dichromate to 100 parts of phosphoric acid, and the concentration of the phosphoric acid being of the order of 10 to 20%, and drying the coated article.

14. The method as set forth in claim 13, in which the dichromate is sodium dichromate.

15. The method as set forth in claim 13, in which the ratio of dichromate to phosphoric acid is of the order of .8 to .9 parts of dichromate to 1 part of phosphoric acid.

16. The method as set forth in claim 13, in which an inert colloidal dispersing agent is applied with said solution whereby a coating of uniform appearance is produced.

17. The method as set forth in claim 13, wherein bentonite is added to the solution.

18. The method as set forth in claim 13, in which 5 to 20% of bentonite is incorporated with the solution.

19. The method as set forth in claim 13, in which the baking is carried out at a temperature of the order of 200° C.

20. A composition of matter suitable for rust-proofing ferrous metal objects comprising approximately 13.3% sodium dichromate, 15% orthophosphoric acid and 71.7% water.

GUY A. MCDONALD.