

UNITED STATES PATENT OFFICE

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RUST PROOFING IRON AND STEEL ARTICLES

No Drawing.

Application filed May 22, 1931. Serial No. 539,412.

It has been known for many years that if iron and steel surfaces are treated with dilute phosphoric acid or certain of its acid salts a strongly adherent insoluble protective coating of phosphates of iron is formed thereon. The coating is somewhat porous and its protective properties are somewhat improved by applying a small amount of a non-volatile oil which is absorbed in and fills the capillary openings in the coating and renders it impervious to air and moisture. Iron and steel surfaces have been treated with various other acids, such as sulfuric, nitric and oxalic acid, generally for the purpose of cleaning or pickling. Incidentally some preserving action may result from such treatment due to the removal of oxides of iron which act as catalysts promoting the oxidation or rusting. Nitric acid, as is well known, produces an effect known as passivity, rendering the iron more resistant to oxidation.

The present invention relates to a method of providing iron and steel surfaces with an adherent protective coating of insoluble oxalates of iron. As stated, oxalic acid has been used for cleaning the surfaces of iron and steel objects and is highly efficient for this purpose because it reacts vigorously with ferric oxid and ferric salts to produce the highly soluble ferric oxalate. It is, however, not extensively used for pickling because it is somewhat more expensive than sulfuric acid and other suitable pickling agents.

In accordance with our invention the oxalic acid is not used or only incidentally serves as a cleaning or pickling agent, the principal purpose and effect of the treatment being to form upon the iron or steel surface a fine grained, strongly adherent and insoluble protective coating of an attractive olive green color.

A suitable treatment in accordance with our invention is as follows:

A treating solution is prepared by dissolving 5 parts of oxalic acid $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ in 100 parts of water and adding to this solution $\frac{1}{2}$ to 1 part of concentrated sulfuric acid and about 1 part of ferric sulfate. The iron or steel article to be coated is immersed in this solution, heated to $95-100^\circ \text{C.}$, and left

until a coating of the desired thickness is formed, say 20-25 minutes. The article is then withdrawn from the solution, washed with water and dried. The resulting coating is, as stated, fine grained, strongly adherent and of an olive green color. It may be oiled with clean lubricating oil or painted or lacquered. It provides an admirable surface for lacquering.

Chemical analysis shows that the coating consists of a complex mixture of oxalates of iron. The coating is highly insoluble and is not attacked by 10% acetic acid or by strong solutions of sodium acetate, whereas the simple ferrous and ferric oxalates are quite soluble in acetic acid and are instantly attacked by sodium acetate and converted into the basic iron acetates.

The treatment specified in the foregoing example is capable of considerable variation and is not difficult to control. In general we prefer to use dilute solutions of oxalic acid, but we have found a wide range of concentrations, for example from about 1% to about 10%, to function satisfactorily. The temperature and time of treatment also may be varied within wide ranges, e. g., from atmospheric temperatures up to 100°C. and for periods of from a few minutes up to several hours. The action is, of course, more rapid at higher temperatures. For instance, instead of the treatment at $95-100^\circ \text{C.}$ for 20-25 minutes, described above, a similar coating may be obtained by treatment at atmospheric temperature for about 90 minutes. The longer the treatment is applied the heavier will be the coating. For instance, in treating an iron or steel surface to be lacquered or painted, a treatment for 5 minutes at $95-100^\circ \text{C.}$ with the solution described above will yield a light coating having excellent rust-proofing properties and providing an admirable surface to receive the paint or lacquer.

If the surface to be treated carries only a little rust, no preliminary pickling is required because the oxalic acid solution will first act upon and dissolve the oxides of iron present and then act on the clean iron, liberating hydrogen, to produce the insoluble

oxalate coating. If, however, the iron is coated with mill scale (Fe_2O_3), it is desirable to give it a preliminary pickling with dilute sulfuric acid or other suitable pickling agent.

It is noted that the treating solution illustrated in the foregoing example contains sulfuric acid and ferric sulfate. These ingredients are not essential, but it has been found that the presence of a small amount of sulfuric acid is of considerable assistance in speeding up the rate of formation of the coating and also in giving a coating of a finer grain than is produced in its absence, and that the presence of ferric ion in the treating solution also increases the rate of reaction. The ferric ion may be added in any suitable form, e. g. as ferric sulfate or as potassium ferri-oxalate. The presence of phosphate in the treating solution has a detrimental effect, tending to produce crystalline, non-adherent coatings.

As stated, the presence of ferric ion in the treating solution is beneficial. It seems to act as a catalytic agent or oxygen carrier. Salts of copper and tin have a similar effect in speeding the rate of reaction. Salts of manganese, however, have not been found to give this beneficial effect.

The coatings are, as stated above, an attractive olive green color. This color may be modified by the addition to the treating solution of substances which form colored insoluble iron compounds. For example, the addition of 1% of potassium ferric cyanide to the oxalic acid solution produces a coating of a blue color due to the formation of Prussian blue.

It will be understood from the foregoing disclosure that the invention is not to be confused with the use of oxalic acid for cleaning or pickling iron and steel surfaces.

We claim:

1. Iron and steel articles having on their surfaces a fine grained, strongly adherent coating of an olive green color, consisting of oxalates of iron and being insoluble in 10% acetic acid and strong solutions of sodium acetate.

2. Process of producing protective coatings on iron and steel articles which comprises subjecting a clean metallic surface thereof to the action of a solution containing from about 1% to about 10% of oxalic acid dihydrate and a relatively small amount of an agent serving to accelerate the formation of the coating of the group consisting of sulfuric acid and a ferric salt at a temperature of from about normal atmospheric temperature to about 100°C . for at least about 5 minutes until a coating of the desired thickness is formed thereon.

3. Process of producing protective coatings on iron and steel articles as defined in

claim 2 in which the solution contains from about $\frac{1}{2}$ to about 1% of sulfuric acid.

4. Process of producing protective coatings on iron and steel articles as defined in claim 2 in which the solution contains a small amount in the neighborhood of 1% of a soluble ferric salt.

5. Process of producing protective coatings on iron and steel articles as defined in claim 2 in which the solution contains from about $\frac{1}{2}$ to about 1% of sulfuric acid and a small amount in the neighborhood of 1% of a soluble ferric salt.

6. A solution for the production of protective coatings on iron and steel articles consisting essentially of water with from about 1% to about 10% of oxalic acid dihydrate and from about $\frac{1}{2}$ to about 1% of sulfuric acid.

7. A solution for the production of protective coatings on iron and steel articles as defined in claim 6 in which the solution contains also a small amount in the neighborhood of 1% of a ferric salt.

8. A solution for the production of protective coatings on iron and steel articles consisting essentially of water with from about 1% to about 10% of oxalic acid dihydrate and a small amount in the neighborhood of 1% of a ferric salt.

In testimony whereof, we affix our signatures.

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DISCLAIMER

1,895,568.—*Leo P. Curtin*, Cranbury, N. J., and *Bernard L. Kline*, Brooklyn, N. Y.
RUST PROOFING IRON AND STEEL ARTICLES. Patent dated January 31,
1933. Disclaimer filed March 11, 1942, by the assignee, *The Western Union
Telegraph Company*.

Hereby enters this disclaimer to claim 8 of the patent.
[*Official Gazette April 7, 1942.*]