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METHOD OF AND SOLUTION FOR PRODUCING A COATED IRON ARTICLE

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This invention relates to a method of producing upon an iron or steel surface a coating of ferrous oxalate formed in situ thereon and substantially integral therewith. The article with such a coating thereon is claimed in a divisional application No. 222,221, filed July 30, 1938, and issued November 22, 1938, as Patent No. 2,137,938.

When an iron or steel surface of an article is submerged in a hot solution of oxalic acid, a coating is formed on said surface. This coating is very fine grained, smooth and adherent, and forms an excellent base for paint, enamel, lacquer or the like. When oxalic acid is used alone, the coating is of an olive greenish color and by chemical analysis is shown to have a composition corresponding quite closely to the formula $\text{FeC}_2\text{O}_4(\text{H}_2\text{O})_2$, and therefore may be termed ferrous oxalate. It is insoluble in acetic acid but is soluble in warm sodium acetate.

When the hot oxalic acid solution comes in contact with the iron surface, some of the iron is dissolved to form ferrous oxalate. This oxalate is so slightly soluble that it requires only a trace thereof to saturate the solution, and thereafter the coating of ferrous oxalate is formed on the surface.

The coating action of an oxalic acid solution upon iron may be accelerated by an oxidizing agent so that it will take place promptly at room temperature. There is a wide choice of oxidizing agents. Strong agents may be employed, and on the other hand a chemical, such as sodium sulphite, frequently referred to as a reducing agent, acts as an oxidizing agent in the oxalic acid and oxalate bath.

Ferric iron, added to the solution in any suitable manner, acts as an oxidizing agent, expediting the coating action of the solution. Ferric sulphate, ferric nitrate, ferric chloride and ferric acetate may be cited as examples of soluble ferric salts which give such acceleration. These salts may be used in widely different proportions, but an amount of the order of 1% may be mentioned as a good working proportion.

Of course, when these salts are introduced into the solution, a substantial amount of ferric oxalate is formed. Ferric oxalate acts as an oxidizing agent and accelerates the coating operation. When a stronger oxidizing agent, such as manganese dioxide or hydrogen peroxide, is used, it oxidizes the small amount of ferrous oxalate which normally saturates the solution, changing it to soluble ferric oxalate, which acts with the stronger agent in oxidizing hydrogen at the surface of work and expediting the coating

action. Additional amounts of ferrous oxalate are dissolved and changed to ferric oxalate until equilibrium is reached.

While the solution is customarily saturated with ferrous oxalate and may contain varying amounts of the highly soluble ferric oxalate, the actual attack on the metal is evidently by the oxalic acid itself, and therefore there must be sufficient oxalic acid employed so that it is present as free acid after the formation of such oxalates as are in the solution. The strength of oxalic acid may vary from $\frac{1}{2}$ of 1% to saturation, but 2% may be cited as one satisfactory working strength. At this or a much greater strength the oxalic acid coats rather than pickles when the solution is heated or when the colder solution is properly accelerated by an oxidizing agent.

Manganese dioxide is worthy of special mention, as the manganese enters into the coating, blackening it and somewhat improving its quality. Hydrogen peroxide is given special mention, as it contains nothing which can remain as a harmful residue in the solution.

Compounds of some metals may be added to the solution and further accelerate the coating action, but that forms no part of the invention which this application is intended to cover, and the claims are not intended to either require or exclude compatible chemicals except as stated therein.

What is claimed is:

1. In the coating of iron and steel articles, the process which comprises exposing a surface of such an article to the action of an aqueous solution containing a substantial amount of ferric oxalate until a coating of substantial thickness forms.

2. In the coating of iron and steel articles, the process which comprises exposing a surface of such an article to the action of an acidulated aqueous solution containing a substantial amount of oxalates of iron until a coating of substantial thickness forms.

3. In the process of claim 2, acidulation of the bath with an organic acid at least as highly ionized as acetic acid in concentration sufficient to prevent hydrolysis of the ferric oxalate but insufficient to produce a substantial pickling action.

4. In the process of claim 2, acidulation of the bath with oxalic acid in concentration sufficient to prevent hydrolysis of the ferric oxalate but insufficient to produce a substantial pickling action.

5. In the coating of iron and steel articles, the process which comprises exposing a surface of such an article to the action of an aqueous acidulated solution having in solution therein substantial amounts of the oxalic acid radical and the ferric ion.

6. In the coating of iron and steel by a solution of oxalic acid and oxalates, the method which

consists in expediting the action of the solution by the inclusion therein of ferric salt.

7. 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.

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