

UNITED STATES PATENT OFFICE

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PRODUCTION OF PROTECTIVE COATINGS ON IRON AND STEEL ARTICLES

No Drawing.

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This invention relates to the provision of firm, non-porous, adherent, insoluble protective coatings on iron and steel articles and comprises a process of treating the surfaces of iron and steel articles to produce such coatings thereon.

The protective coatings in accordance with our invention consist essentially of insoluble compounds consisting essentially of oxalates of iron, formed in situ on the articles by interaction between the iron of the article and ferric oxalate, in a solution or bath which ordinarily is more or less acidified to accelerate the reaction as more fully described hereinafter.

Like most other acids, oxalic acid has occasionally been used for cleaning and pickling iron and steel, and particularly for brightwork. For this purpose it has the disadvantage that its acidity is not as great as that of sulphuric and hydrochloric acids and evolution of hydrogen is not rapid. It does, however, have the advantage of great solvent power for ordinary iron rust; a property to which it owes its well known use for removing rust stains. In pickling and scouring iron, its action in practice is found to be erratic. Under some circumstances it leaves a coating on the iron, which has led to the proposal that it be used for forming a protective coating for iron and steel. Again the action is erratic depending very much upon temperature, concentration, and the presence or absence of other bodies, whether a coating is or is not formed. Where a coating is produced, this is done at the expense of the underlying iron and it is difficult to regulate conditions so that hydrogen evolution will not tear off or disrupt the coating and there shall be no formation of a mud or precipitate in the bath. Ferric oxalate is soluble, but ferrous oxalate, in the absence of other oxalates with which it can form a double salt, is almost insoluble in water.

It has been found that a coating bath consisting of a solution containing mainly ferric oxalate or a soluble ferri oxalate gives good coatings on iron and steel articles with reliable operation. The exact chemical nature of the coating is unknown, but it appears

to be a mixture of complex oxalates in which, empirically speaking, ferrous oxalate seems to predominate. Unlike either ferrous oxalate or ferric oxalate, the material of the coating is insoluble in solutions of weak acids, such as acetic acid (vinegar). It is highly resistant to attack. To the extent that the coating is ferrous oxalate, two-thirds of it can be regarded as coming from the solution and only one-third from the iron of the article being coated. The operation of the ferric oxalate bath is regular and there is not the annoying development of hydrogen to dislodge the coating which is incident to the use of most coating baths of acid nature.

In the use of a bath containing ferric oxalate for coating iron and steel by dipping processes, better and quicker results are obtained if a small amount of free acid, such as sulfuric, phosphoric, oxalic or other suitable acid, is added. All ferric salts, including the oxalates, show a tendency to hydrolyze in water; hydrolysis tending to produce ferric hydroxide in solution or suspension. Ferric oxalate is comparatively poorly ionized and displays little tendency to form free oxalic acid as a result of hydrolysis. The presence of ferric hydroxide is disadvantageous, as tending to contaminate the coating or the metal surface to be coated. It is in particular desirable that there be no inclusion of ferric hydroxide in the coating, since it strongly promotes the rusting of the underlying metal. Also, the reaction whereby ferric-ion reacts with metallic iron to produce ferrous-ion or ferrous oxalate is greatly facilitated by maintaining a certain degree of acidity in the treating solution. The acidulating acid should be one which is at least as highly ionized as acetic acid and may be either an organic acid or a mineral acid.

As has been indicated above, the quantity of free acid in the coating bath should not be sufficient to give free evolution of hydrogen with the iron of the article being treated, i. e. it should not exhibit substantial pickling properties, but on the other hand it should be sufficient to prevent harmful hydrolysis of the ferric oxalate and to promote the formation of the coating. Assuming a ferric

oxalate concentration of about 5%, the use of 0.5% of sulphuric acid in the bath is ample. If oxalic acid is used in place of sulphuric acid, at least 1% is desirable. More oxalic acid may be used, if desired, good results being obtained with the ferric oxalate and oxalic acid present in about equimolecular proportions. A greater proportion of oxalic acid is objectionable because of its interaction with metallic iron and consequent liberation of gaseous hydrogen.

The bath may be replenished as required with ferric oxalate and adjustment of its composition may be accomplished in case of need by suitable additions of oxalic acid or hydrated ferric oxide of a good reactive grade. The coating operation withdraws both iron and oxalate from the bath.

In the present method of coating, the article to be coated is sometimes made the anode, in a solution of ferric oxalate, a moderate E. M. F. being applied. This accelerates the action and greatly reduces the time necessary to obtain satisfactory coatings.

The particular concentration of the bath is not greatly important. Good results are obtained with a coating bath containing 50 parts of ferric oxalate and 25 parts of oxalic acid per liter at a temperature around 90° C. The ferric oxalate may be the ordinary commercial grade used for making blueprints; the yellow-brown scale preparation. The temperature used varies. In general the speed of formation of coating increases as the temperature, but boiling the bath should be avoided. The iron or steel article to be coated is immersed in the bath at a suitable temperature, allowed to remain until a fine grained, satiny coating is obtained, withdrawn, washed and dried. The article can then be used without further treatment, or can be painted, varnished or lacquered. While the coherence of paint, varnish or lacquer to bright iron or steel is not good, the bond of the coating with the underlying metal is excellent and gives good coherence to paint, varnish, etc. The color of the coating is ordinarily olive green when pure chemicals are used. In the presence of foreign metals in the solution, these tend to join the coating to some extent and vary the color. The presence of ordinary rust on the article is immaterial, since with the somewhat acid solution used according to the invention, it goes into solution and joins the bath. The coating action appears to be a straight reduction of ferric oxalate to ferrous oxalate with deposition of the latter in place; it joining the ferrous oxalate formed at the expense of the metal of the article.

In none of the procedures herein described is it necessary to start with the pure dry ferric salt; it is sufficient to produce, by any means, an acidified solution which contains in the proper proportions ferric-ion and the

desired acidic radical which is to form part of the coating. In the bath of ferric oxalate, some ferrous oxalate is always present; this being formed at the expense of the ferric oxalate by reduction in the bath. Its presence is not disadvantageous, but on the other hand it is desirable as long as there is not sufficient to form an insoluble precipitate or mud. Some of the advantages of the present invention may be utilized in coating iron and steel articles with other organic iron compounds, such as the tartrate and salicylate.

The coatings produced by practicing the process of the present invention find many obvious applications in the arts. A special use to which they admirably are adapted is in the preparation of laminations for electromagnets, laminated cores of transformers, and related electrical equipment, serving as an insulating layer or film in place of mill scale or other insulating coating between laminæ. Such equipment, as is well known, is made up of superposed thin, flat pieces of iron, cut to size, mill scale or other insulating material on the contacting surfaces of the pieces serving to insulate them from each other and reduce eddy current losses. It has been found that in a certain transformer core construction in which mill scale serves as the insulator, and in which the electrical resistance perpendicular to the plane of the laminations is 100 ohms, the resistance in an otherwise identical core made up of laminæ coated in accordance with the present invention is 4,000,000 ohms.

We claim:

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

6. In the process of claim 2, acidulation of the bath with sulphuric acid.

7. In the process of claim 2, acidulation of the bath with phosphoric acid.

5 In testimony whereof, we affix our signatures.

LEO P. CURTIN.
BERNARD L. KLINE.

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DISCLAIMER

15 1,895,569.—*Leo P. Curtin*, Cranbury, N. J., and *Bernard L. Kline*, Brooklyn, N. Y.
PRODUCTION OF PROTECTIVE COATINGS ON 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 claims 1, 2, 3, and 4 of the patent.

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[*Official Gazette April 7, 1942.*]

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