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PROCESS OF FORMING OXALATE COATINGS ON IRON AND STEEL ARTICLES

No Drawing. Application filed May 4, 1932. Serial No. 609,277.

In applications Serial Nos. 539,412 and 591,932, filed May 22, 1931, and February 9, 1932, respectively, in the names of Leo P. Curtin and Bernard L. Kline, there are described methods of forming protective coatings on iron and steel articles, involving subjecting the clean surfaces thereof to be coated to the action of solutions containing oxalic acid and ferric oxalate, respectively, as the essential ingredients.

The present invention relates to a method of forming protective coatings on iron and steel articles by the action of baths or solutions of the type disclosed in said applications, but is designed to hasten the formation of the coating or shorten the time required for the production of a given coating. The time element involved in the formation of protective coatings on iron and steel articles is of great economic importance.

In accordance with the present invention the formation of the protective coating is hastened by the action of electric current; that is to say, the article is contacted with the coating bath or solution and electric current is passed through the article, serving as the anode, the bath, and an inert cathode such as a carbon rod.

A variety of coating solutions may be employed which are of three general types: (1) solutions of oxalic acid, (2) solutions of ferric oxalate, and (3) solutions containing both ferric oxalate and oxalic acid in varying proportions. The latter type of bath generally gives slightly quicker results and particularly when the ratio of oxalic acid to ferric oxalate in the bath is within the approximate limits of 5 parts by weight of oxalic acid dihydrate, $C_2H_2O_4.2H_2O$, to from 1 to 5 parts by weight of ferric oxalate hexahydrate, $Fe_2(C_2O_4)_3.6H_2O$.

In general the expedients employed in obtaining coatings without the use of electric current may be used to advantage also when electric current is applied in accordance with the present invention. For instance, if the surface of the iron or steel article is not clean, e. g. oily or greasy or rusty, it may be preliminarily cleaned in any suitable way, as by washing with a solvent for the grease, or by pickling, or, especially in the case of a rusted surface, the coating bath may also serve as the cleaning or pickling bath. Oxalic acid is known to be an efficient pickling agent, but heretofore has not been used extensively for the purpose on account of its cost.

In the use of oxalic acid alone a 5% solution of the dihydrate of oxalic acid is suitable, although more or less concentrated solutions, e. g. from 1 to 10%, may be employed. A small amount of sulfuric acid, e. g. ½ to 1%, or of a ferric salt such as ferric sulfate, e. g. 1% of ferric sulfate may be added to the oxalic acid bath, but this is not essential and is of little or no utility when applying electric current to hasten the formation of the coating in accordance with the present invention. The bath may also be heated, e. g. to 95–100° C., but this expedient also is of less importance in the present process than when the coating is formed without the aid of electric current. In general the hotter is the bath the more rapid is the formation of the coating, but the bath should not be boiled. Heating and the presence of such additions as sulfuric acid and ferric sulfate serve to hasten the formation of the coating, but the effect thereof is practically negligible when the formation of the coating is carried out with the aid of electric current. The thickness of the coating can, of course, be varied by varying the time of treatment. Thin coatings generally are formed when the article is to be painted or lacquered, and serves not only to protect the metal against corrosion, but also to bond the paint or lacquer to the article. Thicker coatings are provided when they are to serve as the sole surface finish. Such coatings may be oiled to render them impervious.

In the use of solutions of ferric oxalate it is desirable to acidify the solutions sufficiently with an acid such as sulfuric or oxalic to prevent hydrolysis of the ferric oxalate and the deposition of insoluble material, such as ferric hydroxide, which may tend to deposit with or upon the coating on the article and damage it. The quantity and strength of acid added to the bath should, however, not be sufficient to react with the metal of the

article and give an objectionable evolution of hydrogen which tends to disrupt the coating. With a 5% solution of ferric oxalate a suitable addition of sulfuric acid is 0.5% and of oxalic acid 1%. The use of oxalic acid as the acidifying acid in a ferric oxalate bath gives baths of type (3) referred to above, in which, however, as stated, the preferred composition is 5 parts of oxalic acid to from 1 to 5 parts of ferric oxalate. A suitable bath concentration is 20 parts by weight of ferric oxalate and 50 parts by weight of oxalic acid per 1000 parts by weight of solution.

The baths referred to may be restored or replenished from time to time as required by the addition of suitable reagents such as ferric oxalate or oxalic acid and in case the ferric oxalate becomes reduced to ferrous oxalate it may be reoxidized by the addition of hydrogen peroxide as described in my companion application, Serial No. 608,143, filed April 28, 1932. In coating from an acidified ferric oxalate bath the iron content of the bath is consumed, while in coating from an oxalic acid bath iron goes into solution, oxalic acid or oxalate radical being consumed in both cases, and the restoring of the bath may therefore require the addition of iron, e. g. as hydrated ferric oxide, or oxalic acid, or both, or ferric oxalate. The potential and current density are not at all critical. Potential of from 0.5 to 2 volts have been found to be quite suitable and current densities of from .005 to .05 amperes per square centimeter, but it may be noted that when the potential is too low the effect becomes negligible, while at high potentials there is a tendency to form ferric oxide instead of the complex oxalate of iron on the surface of the article. A potential of 1.75 volts has been found to give good results. In general the time required to form a coating of a given thickness by the use of electric current is less than half the time required when current is not used. The time required to form a coating depends entirely on the thickness of the coating and it is therefore impossible to state the time required. The thickness of the coatings has not been measured. It may be said, however, that a thin coating suitable for painting generally is formed in five minutes or less and a thick coating adapted to serve alone as the finish on the surface of the article in ten minutes or less. It is noted that the direction of current flow in the coating operation tends to oxidize the article being coated and consequently operates against any tendency which the acid in the coating bath may have to react with the metal of the article with the liberation of hydrogen. Hydrogen liberation at the surface of the article being coated is objectionable because it tends to rupture the coating or leave craters therein.

The chemical composition of the coatings has not been determined. They appear to be complex oxalates of iron, which, unlike the ferrous and ferric oxalates, are insoluble in water and quite resistant to the solvent action of acetic acid and sodium acetate. They are quite firm, relatively non-porous or impervious, and fine grained, strongly adherent and have an attractive olive green color. The coatings formed by the use of electric current are essentially the same as those produced without the use of current.

This application is a continuation-in-part of my application, Serial No. 543,748, filed June 11, 1931.

I claim:

1. Method of hastening the formation of oxalate coatings on the surfaces of iron and steel articles exposed to the action of solutions containing soluble compounds including the oxalate radical which comprises arranging the article to be coated as the anode in an electrical circuit in a bath of such a solution and impressing a potential of about from 0.5 to 2 volts at a current density of about from .005 to .05 amperes per square centimeter on said article.

2. Method as defined in claim 1 in which the bath is a solution of oxalic acid.

3. Method as defined in claim 1 in which the bath is a solution of ferric oxalate.

4. Method as defined in claim 1 in which the bath is a solution containing both ferric oxalate and oxalic acid.

5. Method as defined in claim 1 in which the bath is a solution of oxalic acid and ferric oxalate in the proportions of 5 parts by weight of oxalic acid dihydrate to from 1 to 5 parts by weight of ferric oxalate hexahydrate.

In testimony whereof, I affix my signature.

LEO P. CURTIN.