

1

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METHOD, BATH AND COMPOSITION FOR COATING CORROSION RESISTANT ALLOYS

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This invention relates to the art of coating corrosion resistant alloys and is particularly concerned with a novel method of as well as with an improved bath and a new composition of material for use in coating nickel base alloys such as those known in the art as "Nichrome"¹ and "Inconel"¹ alloys and the various stainless steels such as those referred to as the 200, 300, 400 and 500 series.

Before outlining the objects of the present invention it is desired to refer to certain practices of the prior art because these should be kept in mind in order to fully appreciate and understand the nature of the present invention.

The various commercially available processes for chemically coating nickel base or stainless steel alloys, insofar as I am aware, are all based upon the use of acidic solutions of oxalic acid. The coatings are applied for one reason or another and particularly as an aid in the chipless deformation of such metals. Without exception all of the processes employing oxalic acid are difficult to control and at times necessitate the addition to the bath of as many as five different chemicals or formulations in varying amounts in order to insure reasonably satisfactory operating conditions and the attainment of acceptable results.

Basically considered, these prior art coating processes may be divided into two types, i.e., those requiring solutions containing oxalate and halide ions plus other additives such as a sulfur bearing compound containing oxygen which is capable of yielding sulfur dioxide and sulfur in acid solution and those in which the objectionable halides are eliminated and which require, in addition to the oxalate ions, manganese and free mineral acid ions plus the aforementioned sulfur bearing compounds.

More recently the art has suggested employing solutions containing, in addition to oxalic acid and a sulfur bearing compound such as described above, a water soluble sulfate salt, boric acid or a water soluble borate salt, free sulfur, and a protective colloid such as casein, a gelatin or starch and a wetting agent. Preferred procedure for the process just mentioned requires balancing of the coating bath by constantly bubbling a stream of gaseous sulfur dioxide into the solution. While this process produces satisfactory coatings the bath employed, obviously, is extremely difficult to control.

With the foregoing in mind, the principal object of the present invention may be stated as involving the provision of a process for coating corrosion resistant alloys wherein the baths employed are simple to prepare and equally simple to replenish. A concomitant object is to provide a coating bath or solution and a process with which it is possible to use only one chemical admixture for initial makeup of the bath as well as only a single chemical admixture for its replenishment thereof.

Still further, it is also an object of my invention to

¹ Trademarks for nickel alloys described in "Engineering Alloys" by Woldman as published by ASM 1954 edition.

2

provide dry, free-flowing admixtures of two or more of the chemicals required which admixtures will remain stable in storage for relatively long periods of time without noticeable chemical or physical degradation of any kind.

Other objects include the provision of compositions for use in preparing and replenishing the bath of my invention which will reduce the number of weighing or measuring operations required and thereby minimize the possibility of errors in calculation.

I also contemplate the provision of the required chemicals in forms and compositions which will save shipping space and weight.

The present invention is based upon the discovery that an aqueous solution containing borate and oxalate ions and a sulfur bearing compound containing oxygen, which compound is capable of yielding sulfur and sulfur dioxide in the coating solution, will produce a coating on nickel base alloy surfaces which is exceptionally suited for use in drawing operations.

My work to date indicates that the concentration of oxalate ion in the coating bath should be at least 2 grams/liter and preferably at least 5 grams/liter. Use of less than 2 grams/liter of oxalic acid in the coating bath produces undesirably thin coatings. The upper limit of oxalic acid appears to be controlled, at least with respect to coating quality, by the solubility of the oxalate ion in the acid solution. No apparent detrimental results have been noted when using excessive amounts of oxalic acid. However, in the interest of economy, it is preferred to maintain the oxalic acid concentration between the range of 5 to about 500 grams/liter, the latter concentration being possible when the coating solution is maintained at about 180° F.

The quantity of boric acid should be based on the oxalic acid content and it has been found that as little as 0.1 part to as much as 4.0 parts of boric acid for each part of oxalic acid (weight/weight) may be employed satisfactorily in the coating solutions of this invention. The preferred amount of boric acid is from 0.5 to 2.0 parts for each part of oxalic acid in the coating bath.

The sulfur bearing compounds containing oxygen and which will liberate sulfur and sulfur dioxide in the acid solutions of this invention may be selected from the class of compounds consisting of thiosulfates, sulfites, thionates and hydrosulfites. The amount of sulfur bearing compound to be used in the coating baths should be such that a 10 ml. sample of the bath will react with at least 2 mls. but with no more than 15 mls. of a 0.05 N iodine solution, using starch indicator to a blue endpoint.

Mixtures of sulfur bearing compounds from the class described have been found to be equally useful in the process of this invention so long as the amount of this mixture falls within the titration limits of 2 to 15 mls. of 0.05 N iodine solution as noted above. Use of sulfur bearing compounds in an amount which gives an iodine titration value of less than 2 mls. generally results in a coating which is too thin to be of any practical value in subsequent deforming operations. Employment of an amount of sulfur bearing compounds which exceeds the 15 ml. titration value generally results in a loosely adherent coating which has been found to be predominately of the sulfide type with only small amounts of the desired oxalate coating.

The pH of the coating solutions falls within the range of 0.5 to 2.5 and is preferably maintained within the range of 0.7 to 1.5. It has been found that a solution of oxalic and boric acids and a sulfur bearing compound from the class described generally results in a pH slightly greater than 0.5. Use of coating solutions having pH values of less than 0.5 are undesirable, since the acid solutions begin to exert a noticeable pickling action on

the metal surfaces with accompanying loss of coating ability. Use of coating solutions having pH values greater than 2.5 results in poor coating quality since the surfaces are not sufficiently attacked by the solution to produce a satisfactory coating.

While it has been found that the use of oxalate and borate salts such as the sodium, potassium and ammonium salts are suitable for use in the solutions of this invention, the use of such salts necessitates the addition of acid anions in order to obtain the desired pH range. Accordingly, in the preferred embodiment of this invention the use of oxalic and boric acids per se has been found to result in simple preparation and maintenance of the coating solutions and also makes it possible to use a minimum of chemical admixtures.

In general the coating bath which is used in accordance with the process of this invention may be operated over a temperature range of 120–180° F. Below 120° F. (and the bath may be used below this temperature if desired) the time required to form a satisfactory coating on nickel base alloy surfaces is excessive and impractical from a commercial viewpoint. Use of temperatures above 180° F. results in excessive gas evolution (presumably sulfur dioxide and hydrogen sulfide) which is obnoxious and which unnecessarily wastes coating producing chemicals. However, it has been found that the use of an oil layer over a coating bath, such as described in my co-pending application Serial No. 681,900, filed September 4, 1957, permits the use of oxalate solution temperatures in excess of 180° F. Without the benefit of an oil layer over the coating solution, the preferred operating temperature is between 150 and 160° F.

The surface of the metal article to be coated should be properly cleaned and activated as is sometimes necessary with certain stainless steels prior to introduction in the coating solutions of this invention. In the case of stainless steels which are known to be passive in nature it is generally desirable to subject these to the action of an activating pickling solution. However, since neither the cleaning nor the pickling cycles form any part of this invention, and since both operations are well established in the art they will not be described in detail.

Illustrative examples of coating solutions falling under the purview of this invention are listed below, but are in no way intended to limit the scope of this invention:

Example I

	Grams
Oxalic acid.....	40
Boric acid.....	20
Sodium thiosulfate.....	2.0
Water, to make 1 liter.	

Example II

Oxalic acid.....	4
Boric acid.....	4
Sodium thiosulfate.....	0.5
Water, to make 1 liter.	

Example III

Oxalic acid.....	300
Boric acid.....	30
Sodium thiosulfate.....	1.0
Water, to make 1 liter.	

In the foregoing examples some other sulfur bearing compound or mixtures of compounds from the class mentioned above may be employed just so long as the quantity thereof which may be employed responds to the titration qualifications described.

If, instead of oxalic and boric acid, a soluble salt such as the sodium, potassium or ammonium salt of either boric or oxalic acids, are used in the examples given above, sufficient mineral acid such as sulfuric, hydrochloric, nitric or phosphoric should be added to the bath to reduce the pH to between 0.5 and 2.5.

Dry admixtures for use in preparing and replenishing the coating baths of my invention can be prepared as follows: Boron trioxide is intimately admixed with commercial grade oxalic acid; i.e., oxalic acid with two molecules of hydration. Such an admixture produces a substantially anhydrous composition of coating producing chemicals which will remain substantially free-flowing and powdery even after extended storage and this without noticeable chemical or physical degradation of any kind. The discovery that such a mixture would be dry, free-flowing and stable was quite unexpected because, while boric acid and hydrated oxalic acid are individually stable compounds, when mixed, particularly in the presence of the sulfur compound, chemical degradation and caking occur. On the other hand, my improved admixtures of boron trioxide and hydrated oxalic acid are surprisingly stable compositions even after periods of storage of several months or more. Beyond this, I have found that sulfur bearing compounds from the class consisting of anhydrous sodium and potassium salts of thiosulfate, sulfite, and hydrosulfite can be added to such mixtures of boron trioxide and oxalic acid without producing instability or the development of physical degradation of the admixture and without destroying the anhydrous free-flowing character of the admixture. Such stable admixtures for use in preparing and maintaining an oxalate coating bath have never heretofore been developed insofar as I am aware.

The amount of commercial grade oxalic acid which may be used in formulating the highly stable dry admixtures of this invention is dependent upon the amount of boron trioxide used. I have found that from 0.5 to 1.5 mols of commercial grade oxalic acid may be used for every mol of boron trioxide employed. When admixtures are prepared containing a sulfur bearing compound from the class disclosed, it has been found that the sulfur bearing compound may be present in an amount ranging from 5 to 80% (weight/weight) of the total composition. The boron trioxide may be present in amounts ranging from 5 to 47.5% (weight/weight) of the total composition and the oxalic acid may be present in amounts ranging from 10 to 70% by weight of the total composition.

Baths according to this invention may be initially prepared or subsequently replenished with compositions such as above described. If a composition including only hydrated oxalic acid and boron trioxide is used then of course it will be necessary to add to the bath the requisite quantity of a sulfur bearing compound of the character above described. On the other hand, admixtures containing all three of the basic ingredients may be prepared in accordance with the teachings above set forth and by way of illustration the following examples of dry admixtures useful for the purposes of the present invention are as follows:

Example IV

	Percent by wt.
Oxalic acid ($H_2C_2O_4 \cdot 2H_2O$)	65
Boron trioxide	35

Example V

Oxalic acid ($H_2C_2O_4 \cdot 2H_2O$)	70
Boron trioxide	25
Potassium sulfite	5

Example VI

Oxalic acid ($H_2C_2O_4 \cdot 2H_2O$)	36.5
Boron trioxide	13.5
Sodium thiosulfate	50.0

Example VII

Oxalic acid ($H_2C_2O_4 \cdot 2H_2O$)	32
Boron trioxide	18
Sodium hydrosulfite	50

In operating the oxalate coating solutions of this invention it is to be understood that the coating ingredients are depleted during treatment of a succession of articles. The rate of depletion of the respective constituents in the baths of this invention has been observed to depend upon the manner in which the bath is used.

When the bath is operated on a continuous basis with moderately heavy bath loading, it has been observed that all of the coating producing ingredients are consumed on a relatively uniform basis. Accordingly, replenishment of the bath is most readily and conveniently accomplished by adding a sufficient amount of a dry coating chemical admixture such as shown in Example V above. This will restore the three ingredients to the desired level.

On the other hand, it has been noted that operation of these coating baths at period intervals (such as would occur, for example, in an installation being used for only an 8-hr. daily period), or at excessive temperatures, tends to deplete the sulfur bearing compound at a more rapid rate in comparison to the oxalic and boric acid consumption. Under these operating conditions replenishment of the bath may be accomplished by use of the dry coating chemical admixtures such as shown in Examples VI and VII. However, if desired, it should be understood that the coating baths of this invention may be replenished in the usual manner familiar in the art which consists of adding the individual coating constituents as required.

Replenishment of the coating chemicals is effected in accordance with needs as determined by pointage titration which technique is well known in the coating industry so as to require no elaboration in this description.

It will be obvious from the foregoing that use of my admixtures makes it possible to prepare and maintain a bath by weighing or measuring only one admixture which, of course, reduces the possibility of error in calculation such as often occurs in prior practice where a series of different ingredients are separately weighed and added to the bath. Even in situations where a mixture of oxalic acid and boron trioxide is employed together with the separate addition of a suitable type of sulfur bearing compound, my invention is of distinct advantage because the individual packages containing such materials are each dry, free-flowing and stable in storage and the need to measure only two compounds still presents an advantage insofar as reducing errors is concerned.

I claim:

1. In the coating of corrosion resistant alloys from the class which consists of nickel base alloys and stainless steels, the method which comprises subjecting the surface of the alloy to the action of an aqueous acid solution consisting essentially of oxalate and borate ions and a sulfur bearing compound containing oxygen, which compound is cable of yielding sulfur and sulfur dioxide in the solution; the concentration of oxalate ion in the solution being from 2 to 500 grams/liter, the quantity of borate ion being from 0.1 part to 4.0 parts for each part of oxalate (weight/weight), and the sulfur bearing compound being chosen from the class which consists of thiosulfates, sulfites, thionates and hydrosulfites in an amount such that a 10 ml. sample of the solution will react with at least 2 mls. but with no more than 15 mls. of a 0.05 N iodine solution, using starch indicator to a blue endpoint; the pH of the solution being from 0.5 to 2.5.

2. In the coating of corrosion resistant alloys from the

class which consists of nickel base alloys and stainless steels, the method which comprises subjecting the surface of the alloy to the action of an aqueous acid solution consisting essentially of oxalate and borate ions and a sulfur bearing compound containing oxygen, which compound is capable of yielding sulfur and sulfur dioxide in the solution; the concentration of oxalate ion in the solution being from 2 to 500 grams/liter, the quantity of borate ion being from 0.1 part to 4.0 parts for each part of oxalate (weight/weight), and the sulfur bearing compound being chosen from the class which consists of thiosulfates, sulfites, thionates and hydrosulfites in an amount such that a 10 ml. sample of the solution will react with at least 2 mls. but with no more than 15 mls. of a 0.05 N iodine solution, using starch indicator to a blue endpoint; the pH of the solution being from 0.5 to 2.5, and maintaining the specified content of oxalate and borate ions as the solution is continued in service by adding thereto oxalic acid and boric acid per se in the requisite quantities.

3. A method according to claim 1 wherein the content of borate is from 0.5 to 2.0 parts for each part of oxalate.

4. A method according to claim 3 wherein the pH is maintained from 0.7 to 1.5.

5. A method according to claim 1 wherein the temperature of the solution lies within the range from 120° to 180° F.

6. An aqueous acid metal coating bath, said bath consisting essentially of oxalate and borate ions and a sulfur bearing compound containing oxygen, said compound being capable of yielding sulfur and sulfur dioxide in the bath; the concentration of oxalate ion being from 2 to 500 grams/liter, of borate ion from 0.1 part to 4.0 parts for each part of oxalate (weight/weight) and the sulfur bearing compound being chosen from the class which consists of thiosulfates, sulfites, thionates and hydrosulfites in an amount such that a 10 ml. sample of the bath will react with at least 2 mls. but with no more than 15 mls. of a 0.05 N iodine solution, using starch indicator to a blue endpoint, the pH of the bath being from 0.5 to 2.5.

7. A bath according to claim 6 wherein the content of borate ion is from 0.5 to 2.0 parts for each part of oxalate ion.

8. A dry admixture for use in preparing and replenishing an aqueous acid metal coating bath which admixture consists essentially of oxalic acid and boron trioxide, the quantity of oxalic acid in the mixture being from 0.5 to 1.5 mols for each mol of boron trioxide present.

9. A dry admixture for use in preparing and replenishing an aqueous acid metal coating bath which admixture consists essentially of oxalic acid, boron trioxide and a sulfur bearing compound containing oxygen, said compound being chosen from the class which consists of the anhydrous sodium and potassium salts of thiosulfate, sulfite, and hydrosulfite; the latter being present in an amount ranging from 5 to 80% (weight/weight) of the total admixture, the boron trioxide being present in an amount ranging from 5 to 47.5% (weight/weight) of the total admixture and the oxalic acid from 10 to 70% by weight of the total admixture.

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