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ACTIVATION OF OXALATE METAL COATING COMPOSITIONS

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This invention relates to a coating for the protection of stainless steel during mechanical working operations which result in extensive plastic deformation of the metal and, more particularly, relates to a method of activating the oxalate metal-coating compositions of the art for use on stainless steel during such deformation.

This is a continuation-in-part of my prior application for an Oxalate Coated Article of Corrosion Resistant Metal and Method and Chemical for Making Same, Serial No. 782,966, filed October 29, 1947, which application is now abandoned.

It has been taught that solutions comprising oxalic acid attack certain metal surfaces and produce a coating thereon. Oxalate compositions have been suggested as a base for paints to increase the corrosion resistance of the coated metal and other oxalate solutions have been suggested as so-called "drawing" compositions.

In this latter connection it has been discovered that where the metal is to be drawn or otherwise subjected to deformation, an oxalate coating on the surface aids materially in protecting the surface against injury during such drawing or other deformation.

Not all metals or metal alloys have been found susceptible to the action of the suggested oxalate compositions of the art. As a general rule, metals which resist corrosion will resist the action of oxalate coating compositions. For example; nickel, chromium, and alloys containing as much as 8% of either or both of these two metals, are quite resistant to chemical action and, although a mixture of oxalic acid and ferric oxalate will cause a coating to form thereon, the coating is relatively nonadherent and dusty as compared with the coatings on iron.

It has already been taught that various ingredients may be added to an oxalic acid bath to speed up the reaction of the bath on the metal, as for example, ferric oxalate. These added ingredients, many of which are oxidizing agents, have been called accelerators. However, it is to be recognized that too rapid an attack on the metal may in itself be objectionable. A too rapid attack may cause an active pickling effect and the production of no coating at all. It is, therefore, a considerable problem to increase the activity of a bath against the most resistant stainless steels without destroying the property of the same bath to coat effectively the less resistant metals.

For this reason I prefer to name the new bath ingredients of this invention "activators" in view

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of the fact that they increase the activity of the bath on the most resistant stainless steels and at the same time have no adverse effect on the results secured with the more reactive metals.

I have now found that the chloride ion and several other anions have an activating influence distinct from the accelerating influence of the ferric ion, and improved drawing coatings for stainless steel may be obtained by incorporating chloride ions or their equivalent in an oxalate bath containing proportions of a ferric compound sufficient for effective acceleration on the less resistant metals.

It is, therefore, an object of this invention to provide a method for the activation of oxalate coating compositions in order that the latter will attack and effectively coat any of the stainless steels to produce a coating which will protect the surface of the steel during deformation operations.

It is a further object to provide a metal coating composition having incorporated therein an agent or agents capable of carrying out such activation.

I have now found that the foregoing and related objects can be secured by the use of an acidic aqueous oxalate metal-coating composition comprising a member of the group consisting of oxalic acid and ferric oxalate; an accelerator, preferably the ferric ion; and a member of the group of anions consisting of chloride, bromide, ferricyanide and thiocyanate.

It is a member of the last named group of anions which, when incorporated in the oxalate bath, causes an activation of the coating solution in its action against the most resistant stainless steels and which provides a superior drawing coating and coating method when used with the less resistant metals. Thus, the invention includes a composition for coating a stainless steel to protect the surface during deformation operations such as drawing and the like which comprises an acidic aqueous oxalate metal-coating composition having incorporated therein a member of the group of anions consisting of chloride, bromide, ferricyanide, and thiocyanate in a proportion sufficient to increase the rate of reaction of the composition with the surface of the stainless steel.

Where the accelerator used in ferric oxalate, the mixing of the bath constituents is best carried out by adding ferrous oxalate to an aqueous solution of oxalic acid containing an oxidizing agent. Oxidation of the very slightly soluble ferrous oxalate brings about the solution of the

iron in the form of ferric oxalate. As the proportion of ferric oxalate in the solution increases, the solubility therein of ferrous oxalate increases materially.

Any oxidizing agent may be used to put the ferrous oxalate into solution, but it is preferred that agents which leave no objectionable residue be used. Sodium chlorate is an example of such an oxidizing agent. It is preferred, although not necessary, that the amount of chlorate or other oxidizing agent used be less than that necessary to oxidize all the ferrous ion to ferric ion. When ferrous oxalate partly saturates the ferric oxalate solution, the coating deposits more readily, but at greater concentrations of ferrous oxalate a point is reached where the deposition tends to be loose and not satisfactorily adherent.

When the metal surface is first subjected to the action of the bath, the deposition of coating is relatively rapid. However, a point is reached where there is maximum coating, and after that further processing may reduce the coating. In other words, the rate of etching of the metal and to some extent, the rate of redissolving of the ferrous oxalate in the bath increases in proportion to the rate of deposition of coating as time goes on.

I prefer to use an acidic aqueous solution which comprises about 0.4–15% iron or, more particularly, a solution comprising about 6% iron, about 16% of the oxalate ion and about 2% to 15% chloride ion where the iron and oxalate are derived from a mixture of oxalic acid and ferric oxalate or a mixture of ferric oxalate and a small percentage of an acid other than oxalic acid. It will be apparent in the latter case that hydrolysis of the ferric oxalate will result in the presence of oxalic acid in the solution and it is for this reason that ferric oxalate may serve as a source of the coating ingredients or may serve as an accelerator in an oxalic acid bath.

As one example, a solution was made by dissolving 83 pounds of oxalic acid crystals and 150 pounds of ferrous oxalate in water containing 14 pounds of sodium chlorate. When the solution was completed, 125 pounds of sodium chloride were added and the solution was made up to 100 gallons. This solution was applied in one case for 5 minutes at a temperature of 110° F. to stainless steel having a composition of substantially 18% Cr, 8% Ni and 74% Fe. During use, the acidity was depleted so that oxalic acid was added from time to time to maintain the original acidity. Similarly, additional quantities of chlorate were added to return the precipitated ferrous oxalate to the solution as ferric oxalate.

The solution given in the above example has been used in a range of temperatures from room temperature to its boiling point and has coated all stainless steels available for test purposes, which includes scores of different compositions. The term "stainless steel" is used herein in its generally accepted meaning. A detailed list of steels which come under the term "stainless steels" can be found on pages 554 and 555 of the 1948 edition of the Metals Handbook published by the American Society For Metals.

The solution will operate with less amounts of ferric oxalate as an accelerator, but a weaker solution requires a higher temperature for equivalent results. With the solution given, fair drawing coatings may be produced on stainless steel even at room temperature, whereas with 1.5 g. of ferric iron per 100 ml. of solution, for

example, a temperature of about 170° F. was found desirable. Therefore, while chloride activated compositions including relatively small amounts of ferric oxalate will produce coatings on stainless steels for the purpose of drawing, etc., I prefer to use at least 5 g. of ferric iron in 100 ml. of solution together with an effective proportion of the chloride ion. More ferric oxalate, up to saturation, does no harm.

While particular adjustment of the proportions may be necessary to get the best possible results on different kinds of stainless steel and for different purposes, it will be seen that the coating range covers substantially any reasonable proportion of oxalic acid and accelerator with an effective proportion of the activating anion.

The determination of the best proportion and the minimum effective proportion of chloride ion or equivalent anion can be made for any particular alloy by a few routine tests prior to a commercial installation of the process. As indicated above, the relative resistance of the metal to chemical action is the most important single factor in determining the best percentage. Further and as already indicated, a solution containing at least about 2% chloride ion or equivalent anion is an effective proportion with any of the stainless steels.

Since the exact minimum effective proportion of the anion used will vary somewhat with the proportions of oxalic acid and accelerator used, it may be given as a general rule that in the case of each specific alloy the effective proportion of activating anion may be determined by the increased rate of chemical attack on the metal due to the presence of the anion. Thus, an effective proportion of the chloride ion, the bromide ion, the ferricyanide ion or the thiocyanate ion for the coating of a stainless steel is that proportion which increases the rate of the chemical reaction of a particular oxalate metal-coating composition with the surface of the stainless steel.

In all cases the solution may be analyzed from time to time and the various ingredients added as found necessary.

The dry chemicals as listed above, except sodium chlorate, or their equivalents according to the principles set forth herein may be mixed in about the proportions given and used to make up a coating solution, or the chemicals may be first dissolved and reacted in a limited amount of water and then diluted for use. For replenishing, a smaller proportion of chloride is needed than in making up a new solution. Since some ferrous oxalate formed in the coating operation fails to adhere firmly to the metal being coated and tends to saturate the solution and form sludge, such ferrous oxalate may be reoxidized and therefore relatively reduced amounts of ferrous oxalate are required in replenishing. Therefore, whether introduced as a concentrated solution, as mixed dry chemicals, or as separate chemicals, replenishment is ordinarily by oxalic acid and chloride. Sodium chlorate, hydrogen peroxide or other suitable oxidizing agent may be added in an amount to oxidize the desired quantity of ferrous oxalate to ferric oxalate.

The chloride ion and the other anions may be supplied in any form except that it is preferred to avoid the addition of certain cations with the chloride where there is an incompatibility of the cation with the bath ingredients. The compatible salts include those of potassium, lithium, ammonium, magnesium, tin, vanadium, manganese and iron. The salts of chromium may be

used to some extent and are present whenever the solution is employed upon a surface containing chromium, but the amount of these salts should be limited, if the strength of the coating chemicals is low.

Calcium salts precipitate a sludge, probably calcium oxalate, and salts of zinc, cobalt, copper and nickel have a similar tendency. Cadmium chloride has a low degree of ionization and a large proportion is required to yield the effective proportion of chloride ions. Aluminum salts in any great proportion change the coating action. Obviously, any salt of a metal which would cause a precipitation of the metal as an insoluble oxalate would not be a desirable source of the activating anions.

The usefulness of the coating in drawing or deformation in some instances is increased by liming, or dipping in a slurry of hydrated lime. In the commercial drawing of stainless steel to form tubes or wires it has been the practice to coat the metal with lead or with repeated layers of organic dope prior to the drawing. Equally good results can be obtained with oxalate coatings in less time-consuming treatments at much less cost and with the elimination of many difficulties incident to the dope or lead processes. The new method requires merely the formation of the oxalate coating, after which the metal may be worked with the application of suitable drawing compounds such as soap. After drawing, the coating can be easily removed by immersing the work for a short time in an acid pickle. However, with some lubricants it has been found desirable to immerse the coating in an alkaline cleaner prior to the acid pickle.

I claim:

1. A composition of matter for coating a stainless steel to protect the metal surface during a deformation operation such as drawing and the like, comprising essentially an acidic aqueous solution of oxalic acid, a proportion of ferric oxalate yielding about 0.4% to 15% iron and at least about 2% of the chloride ion.

2. A composition of matter for coating a stainless steel to protect the metal surface during a deformation operation such as drawing and the like, comprising essentially an acidic aqueous solution of oxalic acid, about 6% ferric ion and at least about 2% of the chloride ion.

3. In a method of subjecting a stainless steel to deformation such as by drawing and the like; the steps of subjecting, until a substantial coating forms, the surface of the stainless steel to the action of an acidic aqueous solution comprising essentially oxalic acid, ferric oxalate, and at least about 2% of the chloride ion; and thereafter subjecting the stainless steel to said deformation.

4. In a method of subjecting a stainless steel to deformation such as by drawing and the like; the steps of subjecting, until a substantial coating forms, the surface of the stainless steel to the action of an acidic aqueous solution comprising essentially oxalic acid, the ferric ion, and at least about 2% of the chloride ion; and thereafter subjecting the stainless steel to said deformation.

5. In a method of subjecting a stainless steel to deformation such as by drawing and the like; the steps of subjecting, until a substantial coating forms, the surface of the stainless steel to the action of an acidic aqueous solution consisting essentially of oxalic acid, the ferric ion, and the bromide ion, the bromide ion being present in an amount equivalent to at least about 2% of the chloride ion; and thereafter subjecting the stainless steel to said deformation.

6. In a composition of matter for coating a stainless steel to protect the metal surface during a deformation operation such as drawing and the like and comprising essentially an acidic aqueous solution of oxalic acid, the ferric ion and the bromide ion in an amount equivalent to at least about 2% of the chloride ion.

7. In a method of subjecting a stainless steel to deformation such as by drawing and the like; the steps of subjecting the surface of the stainless steel, until a substantial coating forms, to the action of an acidic aqueous solution consisting essentially of oxalic acid, the ferric ion and an anion selected from the group consisting of chloride and bromide, the oxalate ion being present in an amount in excess of that required to form ferric oxalate, the ferric ion being present in an amount between about .4% and 15%, the chloride ion, when present, being present in an amount of at least about 2%, the bromide ion, when present, being present in an amount equivalent to at least about 2% chloride; and thereafter subjecting the stainless steel to said deformation.

8. A composition of matter for coating a stainless steel to protect the metal surface during a deformation operation such as drawing and the like which consists essentially of an acidic aqueous solution of oxalic acid, the ferric ion, and an anion selected from the group consisting of chloride and bromide, the oxalate ion being present in an amount in excess of that required to form ferric oxalate, and the ferric ion being present in an amount between about .4% and 15%, the chloride ion, when present, being present in an amount of at least about 2%, said bromide ion, when present, being present in an amount equivalent to at least about 2% chloride ion.

9. A composition of matter for coating a stainless steel to protect the metal surface during a deformation operation such as drawing and the like consisting essentially of an acidic aqueous solution of oxalic acid, the ferric ion, and at least about 2% of the chloride ion.

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