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2,805,969

MOLYBDENUM ACCELERATED SOLUTION AND METHOD FOR FORMING OXALATE COATINGS ON METALLIC SURFACES

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The present invention relates to a method and a composition for producing coatings on metallic surfaces which are useful in increasing the resistance to corrosion as a base for paint and for protecting the metal surface during mechanical working operations such as drawing and the like.

The use of chemical coatings on metal surfaces as an aid in protecting the metal surface during metal working operations, has long been known and is now rather common. For this purpose, phosphate coatings and oxide coatings as well as oxalate coatings have been proposed. Oxalate coatings have been particularly useful on metals which are difficultly coated such as the stainless steels, chromium nickel alloys, chromium iron alloys, nickel iron alloys, etc. Heated aqueous oxalic acid solutions form coatings on mild steel surfaces, but must be accelerated or activated before oxalate coatings can be formed on the more difficultly coated metals. Accelerators which have been heretofore proposed to increase the attack of oxalic acid on these difficultly coated metals include the conventional oxidizing agents such as hydrogen peroxide, manganese dioxide, sodium sulfite and the ferric ion. Activating anions which have been proposed for use in combination with the ferric ion in U. S. Patent 2,577,887, include one selected from the group consisting of chloride, bromide, thiocyanate and ferricyanide.

The compositions of this invention are of the general type disclosed in U. S. Patent 2,577,887 and are useful in producing adherent oxalate coatings on a wide variety of metallic substrates including mild steel, stainless steel, zinc, aluminum, nickel, copper, chromium and the alloys thereof. The compositions of this invention differ from those of U. S. Patent 2,577,887 in that they include as the activating metallic ion, molybdenum rather than the ferric ion. The preferred compositions include in addition, a conventional oxidizing agent. Molybdenum has been found to be unexpectedly effective in increasing the rate of attack of oxalic acid on the metal substrates listed above. Broadly, the composition of this invention comprises as the essential coating-producing ingredients, molybdenum and an aqueous acidic solution of oxalic acid in a concentration of at least about 4%. In its preferred form the composition of this invention comprises as the essential coating-producing ingredients, molybdenum, an oxidizing anion, an activating halide and an aqueous solution of oxalic acid in a concentration of at least about 4%, the oxidizing anion being present in an amount equivalent to about .05% to 1% chlorate anion, and the activating anion being present in an amount equivalent to about 3.6% to 12.1% chloride.

Metal substrates to which the compositions of this invention have been found to be applicable and to produce adherent oxalate coatings thereon, include mild steel, stainless steel, iron, copper, aluminum, nickel, chromium, zinc and their alloys. Alloys which are specifically contemplated by this invention, include copper-tin alloys, lead-tin alloys, copper-zinc alloys, iron-nickel alloys, iron-chromium alloys, iron-nickel-chromium alloys, nickel-chromium alloys, iron-aluminum alloys. The term "stainless steel" is used herein in its generally accepted meaning. A detailed list of steels which come under the term

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"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 presence of molybdenum in an aqueous acidic oxalic acid solution has been found to accelerate the rate of attack of that solution on mild steel surfaces so that satisfactory adherent oxalate coatings can be produced at lower temperatures and in shorter periods of time than in the absence of molybdenum. Any finite proportion of molybdenum has been found to increase the rate of attack and for this reason no exact lower limit can be stated. For example, quantities of molybdenum as low as 0.025% in an aqueous acidic oxalic acid solution lower the temperature and decrease the time required to obtain an oxalate coating on a mild steel surface. As the proportion of molybdenum is increased, the temperature and time required to form an adherent oxalate coating are decreased.

When the metal to be coated is one which is more resistant to attack by oxalic acid than mild steel or the like, it has been found that the composition for coating the metal surface preferably contains an activating anion in addition to molybdenum. For coating stainless steels, for example, the composition preferably includes at least about 4% oxalic acid, at least about .025% molybdenum and at least about 3.6% chloride anion or its equivalent. Anions which may be used to replace the chloride anion are discussed more fully hereinafter. A preferred composition suitable for coating stainless steels or other metals which are coated only with difficulty, is set forth in Formula I.

FORMULA I

	Percent
35 Molybdenum -----	1-4
Oxalic acid -----	8-20
Chloride anion -----	4.8-9.1

The composition of Formula I produces an adherent oxalate coating which is relatively light in weight and especially suitable for use as a base for paint. The coating is overlaid with an extremely light layer of less adherent oxalate which is generally referred to as the dust portion of the coating. This dust portion can be readily removed by lightly wiping the surface with a cloth, and the adherent portion of the coating which remains on the surface provides corrosion protection to the metal surface when covered with a conventional finish coating of paint, varnish, lacquer, or the like.

Where it is desired to provide heavier coatings which are useful in protecting the metal surface during deformation operations such as drawing and the like, it has been found that such heavier coatings are produced from the above types of solutions if a small quantity of an oxidizing agent is added thereto. Suitable oxidizing agents which may be employed include chlorate, nitrate, nitrite, sodium meta nitro benzene sulfonate, picric acid, cane sugar, potassium dichromate, potassium bromate and hydrogen peroxide. A composition suitable for forming relatively heavier coatings on any of the above metal substrates, is given in the following formula:

FORMULA II

Material	Concentration Useful Range, Percent	Concentration Preferred Range, Percent
65 Molybdenum -----	.025-9	1-4
Oxalic Acid -----	about 4% to saturation	8-20
70 Chloride -----	3.6-12.1	4.8-9.1
Chlorate -----	.05-1	.25-.8

The proportions of other oxidizing agents which may be employed in the place of chlorate in the compositions of Formula II are given in the following table:

Table I

	Concentration Range, Percent
Nitrate -----	.15-15
Nitrite -----	.07-3.5
Picric acid -----	.1-2.1
Sodium meta-nitro benzene sulfonate -----	.05-2
Cane sugar -----	1-9.4
Potassium bromate -----	.1-2.1
Hydrogen peroxide -----	.002-2
Potassium dichromate -----	About .1

The compositions of this invention and especially as the operating temperature is increased, tend to react with and to be decomposed by chlorate, nitrate, nitrite, bromate, peroxide and dichromates at concentrations above those indicated in Table I. A slight amount of interreaction occurs between the oxalic acid and these oxidizing agents even within the range of concentration given in Table I, but the amount is relatively slight and the major effect is a large increase in the coating which is formed. Picric acid does not have the tendency to react with oxalic acid and is therefore preferred.

Activating anions which may be used in the composition set forth in Formula I are the bromide ion and the thiocyanate ion. The bromide ion is useful in concentrations between about 20% to 31% and the preferred range is 22% to 26%. Thiocyanate ion is a suitable replacement for the chloride anion at concentrations of 1% to 22% with most of the benefits being obtained at concentrations between about 1% and 5%. It will be understood that the proportions of bromide and thiocyanate ion which are given, represent those quantities which produce an effect on the coating characteristics of the solution which are comparable or equal to the effect caused by the chloride anion in the quantities set forth in Formula I. The fluoride ion, and ferricyanide ion have not been found to be suitable activators in combination with molybdenum, but these ions in the compositions do not inhibit the formation of coating. Good activating effect was noted with concentration of iodide ion above about 54%, but because of the quantity required, its use is not recommended.

Molybdenum can be introduced into the composition of this invention as molybdic acid or as any salt of molybdic acid, the cation portion of which is compatible with the solution. The alkali metal salts of molybdic acid such as the sodium and potassium salts are typical examples of compatible salts which are sufficiently soluble to provide the necessary concentration of the molybdenum ion.

The examples below are given to more clearly illustrate the compositions and the method of this invention. Proportions of ingredients are given in percentage by weight per volume unless otherwise specified herein, as well as in the appended claims.

EXAMPLE I

A solution was made up by admixing 100 grams $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, 150 grams sodium chloride and sufficient water to make 1 liter. To this solution, various amounts of molybdic acid were added to produce concentrations of molybdenum of 1%, 2%, 3%, 4% and 5%. Type 302 stainless steel panels were immersed in the solution having a temperature of 150° F., maintained therein for 2 minutes and withdrawn. Green adherent relatively light weight coatings were formed from each of the so-

lutions with the coating weights obtained being as follows:

5	Molybdenum Concentration	Dust Coat- ing Weight, Mg./sq. ft.	Adherent Coating Weight, Mg./Sq. ft.
	1.0% -----	12.0	13.0
	2.0% -----	28.8	39.6
10	3.0% -----	30.0	55.2
	4.0% -----	80.0	62.0
	5.0% -----	95.5	91.5

EXAMPLE II

15 A solution was made up containing 10% oxalic acid and 15% sodium chloride. Quantities of molybdic acid were added to produce concentrations of molybdenum of .5%, .75% and 2.7%. Upon immersing type 302 stainless steel panels in the solutions for 5 minutes at 170° F., it was observed only a trace of coating was produced from the solution containing .5% molybdenum, but good coatings were produced from the solutions containing .75% molybdenum and 2.7% molybdenum ion. To a portion of the base solution sodium chlorate was added to produce a concentration of chlorate anion of .05%, and molybdic acid was added in small quantities to establish the threshold quantity of molybdenum which was necessary to produce a coating on type 302 stainless steel panels upon immersion in the solution for 5 minutes at 170° F. Solutions containing less than .025% molybdenum failed to produce a coating. A relatively light weight coating which was suitable for use as a base for paint, was produced from the solution containing .025% molybdenum.

EXAMPLE III

40 An aqueous solution was prepared containing 15% sodium chloride and 1% molybdenum. To this solution varying quantities of oxalic acid were added and 302 type stainless steel panels immersed therein to determine the lower limit of oxalic acid necessary to produce an oxalate coating. Solutions containing less than about 4% oxalic acid failed to produce a coating whereas solutions containing above 4% formed desirable adherent greenish oxalate coatings. Somewhat heavier coatings were formed at oxalic acid concentrations above about 8% and up to about 20%.

EXAMPLE IV

50 A solution was prepared containing 20% oxalic acid, 5.0% molybdenum, 15% sodium chloride and 5% sodium nitrate. Type 302 stainless steel panels were immersed in the solution for 2 minutes at 150° F. and a heavy greenish oxalate coating was formed.

55 To other portions of the solutions containing 20% oxalic acid, 15% sodium chloride, and 5% molybdenum, quantities of sodium nitrate were added to produce concentrations of 2% and 3% and the resultant coatings formed under identical conditions were exceptionally hard and adherent and accompanied with a minimum of loose coating. These coatings were found to be especially suitable as a base for paint and for wear resistance.

EXAMPLE V

65 A solution was prepared containing 20% oxalic acid, 15% sodium chloride and 5% molybdenum. Sodium chlorate was added to portions of this solution to produce concentrations of chlorate ion of .05%, .1%, .5%, 1% and 5%. Type 302 stainless steel panels were immersed in each of these solutions for two minutes at 150° F. Satisfactory coatings were produced from the solutions having concentrations of chlorate anion between .05% and 1%, but at concentrations above 1% chlorate the acceleration decreases rapidly and the oxalic acid is decomposed.

EXAMPLE VI

A solution was prepared containing 10% oxalic acid, 15% sodium chloride and 2.7% molybdenum. With the bath maintained at 150° F., panels of a wide variety of metals and alloys were processed therein for 5 minutes and removed. The metals with this solution include nickel, aluminum, zinc, mild steel, copper, terne alloy, chromium, Monel metal (67% nickel, 28% copper, 1-2% manganese, 1.9%-2.5% iron), Inconel metal (14% chromium, 78% nickel, 8% iron), Ambroloy #901 (95% copper, 5% aluminum), Croloy alloys—Type 310 (25% copper, 20% nickel, balance iron), Everdur alloy (96% copper, 1% manganese, 3% silicon) and Jelliff alloy C (15% chromium, 60% nickel, 25% iron). Typical oxalate coatings were produced on each of the panels. Coatings on copper and brass were relatively light weight thin coatings. The coatings on Monel were heavy and exceptionally adherent.

What is claimed is:

1. A composition of matter for producing an oxalate coating on a metallic surface which comprises an aqueous acidic solution consisting essentially of molybdenum in an amount between about .025% and 9%, oxalic acid in an amount between about 4% to saturation and the chloride anion in an amount of about 3.6% to about 12.1%.

2. A composition of matter for producing an oxalate coating on a metallic surface which comprises an aqueous acidic solution consisting essentially of molybdenum in an amount between about .025% to 9%, oxalic acid in an amount between about 4% and saturation, the chloride anion is an amount between about 3.6% and 12.1% and the chlorate anion in an amount between about .05% and 1%.

3. A composition of matter for producing an oxalate coating on a metallic surface comprising an aqueous solution consisting essentially of 1% to 4% molybdenum, 8% to 20% oxalic acid, 4.8% to 9.1% chloride anion and .25% to .8% chlorate anion.

4. The method of forming an oxalate coating on a metallic surface selected from the class consisting of iron, aluminum, nickel, chromium, zinc, lead, tin and their alloys which comprises the steps of contacting the surface with an aqueous acidic solution consisting essentially of molybdenum in an amount between about .025% and 9%, oxalic acid in an amount between about 4% to satu-

ration and the chloride anion in an amount of about 3.6% to about 12.1%.

5. The method of forming an oxalate coating on a metallic surface selected from the class consisting of iron, aluminum, nickel, chromium, zinc, lead, tin and their alloys which comprises the steps of contacting the surface with an aqueous acidic solution consisting essentially of molybdenum in an amount between about .025% and 9%, oxalic acid in an amount between about 4% and saturation, the chloride anion in an amount between about 3.6% and 12.1% and the chlorate anion in an amount between about .05% and 1%.

6. The method of forming an oxalate coating on a metallic surface selected from the class consisting of iron, aluminum, nickel, chromium, zinc, lead, tin and their alloys which comprises the steps of contacting the surface with an aqueous solution consisting essentially of 1% to 4% molybdenum, 8% to 20% oxalic acid, 4.8% to 9.1% chloride anion and .25% to .8% chlorate anion.

7. A composition of matter for producing an oxalate coating on a metallic surface which comprises an aqueous acidic solution consisting essentially of molybdenum in an amount between about 0.025% and 9%, oxalic acid in an amount between about 4% to saturation and an anion selected from the group consisting of about 3.6% to 12.1% chloride ion, about 20% to 31% bromide ion and about 1% to 22% thiocyanate ion.

8. The method of forming an oxalate coating on a metallic surface selected from the class consisting of iron, aluminum, nickel, chromium, zinc, lead, tin and their alloys, which comprises the steps of contacting the surface with acidic solution consisting essentially of molybdenum in an amount between about 0.025% and 9%, oxalic acid in an amount between about 4% to saturation and an anion selected from the group consisting of about 3.6% to 12.1% chloride ion, about 20% to 31% bromide ion and about 1% to 22% thiocyanate ion.

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