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## METHOD OF COATING

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This invention relates to the field of the chemical coating of metals. An object of the invention is the rendering of metallic surfaces resistant to corrosion. A further object of the invention is to form on metallic surfaces a chemical coating which resists corrosion when coated with a paint, lacquer, or enamel and provides a base coat to which the applied coatings adhere in a much firmer manner than they would to the bare metal.

Generally speaking, the invention comprises the use of solutions containing a soluble hexavalent chromium compound, an oxidizing agent, and a metal etching acid or soluble salt of such an acid on the surface of a metal such as iron, steel, aluminum and their alloys. It is not essential that all of the above ingredients be present in the treatment solution, but in most cases it is advisable in order to get the best results. In some cases it is possible to use chemicals which combine all these features in two compounds for instance, chromic acid used with nitric acid or a nitrate. Here the soluble chromium compound is present and the nitric acid or the nitrate furnishes both the etching agent and the oxidizing agent.

While chromic acid and other hexavalent chromium compounds may be used with metal etching acids or salts of such acids to obtain corrosion resistant coatings without the use of an oxidizing agent other than the hexavalent chromium compound, the addition of another oxidizing agent gives improved results from the stand-points of time, coating properties, hardness, uniformity, and corrosion resistance.

Generally speaking, all the solutions should contain at least a small amount of free acid.

In most cases, on the metal treated in these solutions a coating results which is composed of a substantially insoluble compound of the metal treated and contains some chromium.

A coating analysis made of scrapings from steel panels processed in several solutions appear below:

Solution: $CrO_3+H_2SiF_6+NaNO_3$

| | Percent |
|---|---|
| Fe | 40.48 |
| F | 13.00 |
| Cr | 10.28 |
| $Cr^{VI}$ | 0 |
| Si | .35 |

Solution: $CrO_3+MnSiF_6+NaNO_3$

| | Percent |
|---|---|
| Fe | 54.18 |
| Cr | 4.15 |
| Mn | .61 |
| F | 14.92 |

Solution: $CrO_3+NaNO_3$

| | Percent |
|---|---|
| Fe | 49.45 |
| Cr | 5.10 |
| $Cr^{VI}$ | 0 |

Solution: $CrO_3+H_2SiF_6+NaNO_3+H_2C_2O_4$

| | Percent |
|---|---|
| F | 10.98 |
| Fe | 38.29 |
| Cr | 10.46 |
| $C_2O_4$ | 1.90 |
| Si | .05 |

Solution: $CrO_3+NaNO_3+NaH_2PO_2$

| | Percent |
|---|---|
| Fe | 31.09 |
| Cr | 8.51 |
| $PO_4$ | 44.86 |

It will be noted from the first and third of the above analyses that the chromium in the coating is largely or entirely in the trivalent form, although the chromium is introduced into the treating solution only in the hexavalent form. Obviously, the chromium is reduced from the hexavalent to the trivalent form during the formation of the coating.

In general, any soluble hexavalent chromium compound may be employed, such as chromic acid, soluble salts of chromic acid and other soluble compounds containing chemically combined hexavalent chromium. Oxidizing agents in general may be employed including nitrates, persulphates and the like. Etching acids in general may be employed including hydrofluosilicic, sulphuric, hydrochloric, nitric, oxalic, succinic and the like.

One ordinary method of operation is to immerse the metal in an aqueous solution containing the above ingredients, preferably at elevated temperatures for from one to five minutes, removing the metal from the solution and rinsing with water. At or near boiling temperatures are preferred. Other conditions and methods of operating may be employed within the skill of the art without departing from the spirit of the invention. Time, temperature and other factors may be varied.

An important thing to note is the effect of the negative ions of compounds used in this invention. In combination with a soluble hexavalent chromium compound, in general, wherever the $SO_4$ ion is present an oxide coating results; on iron or steel a black oxide coating results; on aluminum a white oxide coating, and on zinc a light colored coating. This will result where sulphuric acid, any metal sulphate or persulphate is present, and it seems to make very little difference what positive ion accompanies the $SO_4$. Chlorides, on the other hand, produce an altogether different result, although consistently alike in all cases where chlorides are present. Silicoflurodies likewise work alike though differently from chlorides and sulphates.

The following examples will serve to illustrate types of solutions used. These are given merely by way of illustration and not limitation, the scope of the invention being measured only by the claims.

*Example 1.*—A steel object was immersed for 5 minutes in a boiling 200 cc. solution containing 1 gram chromic acid and 1 gram of tartaric acid. A soft, loose, light brown coating was obtained on the metal. In a second experiment, 2 grams sodium nitrate was used with the other ingredients and a thicker coating was obtained on the metal.

*Example 2.*—1 gram of chromic acid, 3 grams of oxalic acid and 2 grams sodium nitrate were used in the manner described in Example 1.

*Example 3.*—A steel object was immersed in a boiling 200 cc. solution to which was added ½ gram chromic acid, 5 grams salicyclic acid and 2 grams sodium nitrate. An iridescent, dark coating was obtained on the metal.

*Example 4.*—A steel object was immersed in a boiling 200 cc. solution to which had been added 1 gram of chromic acid and 10 grams of ferric oxalate. After 5 minutes the metal had an iridescent, shiny coating. Another similar experiment was carried out with 1 gram chromic acid, 2 grams ferric oxalate and 2 grams sodium nitrate under the same conditions. The metal carried a black adherent coating under a heavy soft brown top coating.

*Example 5.*—A steel object was immersed in a boiling 200 cc. solution to which was added 2 grams potassium dichromate, 5 grams manganese silicofluoride and 1 cc. nitric acid. After 5 minutes a black, adherent coating was obtained on the metal. This was improved in a second experiment under the same conditions using a solution to which was added 2 grams potassium dichromate, 5 cc. hydrofluosilicic acid and 2 grams sodium nitrate.

*Example 6.*—A steel object was immersed for 5 minutes in a boiling 200 cc. solution to which was added 2 grams sodium chromate, 1 cc. sulphuric acid and 2 grams nickel sulphate. A soft black coating was obtained. When this experiment was repeated with 2 grams sodium nitrate a good adherent black oxide coating was obtained.

*Example 7.*—A steel object was immersed for 5 minutes in a boiling 200 cc. solution to which was added 4 grams potassium chromate, 10 cc. hydrofluosilicic acid and 2 grams manganese nitrate. An excellent black adherent coating was obtained.

*Example 8.*—A steel object was immersed for 30 minutes in a boiling 200 cc. solution to which had been added 2 grams chromic acid and 3 cc. hydrofluosilicic acid. A dark gray fairly hard coating was obtained on the metal. Another steel object was treated in a similar solution containing one gram of chromic acid, 2½ cc. hydrofluosilicic acid and 2 grams sodium nitrate for 5 minutes. A black adherent coating was obtained under brown dust.

*Example 9.*—A steel object was immersed for 5 minutes in a boiling 200 cc. solution to which had been added ½ gram chromic acid, 1 cc. phosphoric acid and 2 grams sodium nitrate. A thin, light gray coating was obtained on the metal.

*Example 10.*—Under conditions similar to the preceding example a steel object was treated for 5 minutes in a solution containing ½ gram chromic acid, 5 cc. chloric acid ($HClO_3$). A black oxide coating was obtained. A similar experiment was carried out using ½ gram chromic acid, 2 cc. chloric acid and 2 grams sodium nitrate. A good brown and black adherent coating was obtained. When perchloric acid ($HClO_4$) is used in place of chloric acid, similar results are obtained.

*Example 11.*—A steel object is immersed for 5 minutes in a boiling 200 cc. solution to which has been added one gram chromic acid, 2 grams cadmium sulphate and 2 grams sodium nitrate. A hard, adherent, magnetic oxide coating is obtained. When cadmium nitrate is used in place of the sodium nitrate similar results are obtained.

*Example 12.*—Under similar conditions given in the preceding example 2 grams of chromic acid, 5 grams manganese silicofluoride and 2½ grams sodium nitrate were used. A black adherent good coating was obtained in 1 to 5 minutes. This was also true where ferric silicofluoride was used in place of manganese silicofluoride and also where manganese nitrate replaced sodium nitrate.

*Example 13.*—A steel object was immersed for 5 minutes in a boiling 200 cc. solution to which had been added one gram of chromic acid, 2 grams aluminum sulphate and 2 grams sodium nitrate. A good black magnetic oxide coating was obtained. This was also true where tin chloride replaced the aluminum sulphate and also where aluminum nitrate replaced the sodium nitrate.

*Example 14.*—A steel object was immersed for 5 minutes in a boiling 200 cc. solution to which had been added 2 grams chromic acid, 1 cc. hydrogen peroxide and 2 grams sodium nitrate. A black dull coating was obtained.

*Example 15.*—Under conditions similar to the preceding example 2 grams chromic acid, 1 gram potassium persulphate and 2 grams sodium nitrate were used. A heavy black smooth uniform coating was obtained. Similar results were obtained with one gram potassium permanganate instead of the potassium persulphate.

*Example 16.*—Under conditions similar to the preceding example 1 gram chromic acid was used with 5 grams barium nitrate. A light soft coating was obtained.

*Example 17.*—Under similar conditions to the preceding example when 1 gram chromic acid with 10 grams zinc nitrate was used a black, heavy, fairly hard coating was obtained.

*Example 18.*—With one gram chromic acid, 2 grams lead nitrate a black, fairly adherent coating was obtained.

*Example 19.*—When one gram chromic acid and 5 grams ferric nitrate were used a good, hard, dark, iridescent coating was obtained.

In place of the acids mentioned in the above examples other specific acids which were used with chromic acid and chromic acid salts with and without accelerating agents such as nitrates are: sulphurous, molybdic, tungstic, phosphorous, hydrochloric, boric, succinic, gallic, benzene sulphonic, tannic, benzoic, and malonic. Acid salts other than those mentioned in the examples which have been used with chromic acid and/or chromic acid salts with accelerating agents such at nitrates are: Ferrous silicofluoride; sulphates of potassium, sodium, manganese, cobalt, zinc, copper, antimony, silver and aluminum; tin chloride, zinc chloride, aluminum chloride, cadmium chloride sodium chloride, sodium dihydrogen phosphate, calcium dihydrogen phosphate, sodium molybdate, sodium tungstate, potassium chlorate, sodium tetra borate, sodium hypophosphite, potassium bitartrate, manganese gallate, manganese succinate, sodium benzoate, ferric oxalate.

Salts of chromic acid which have been used to replace all or part of the chromic acid of the above examples are: potassium chromate, potassium dichromate, and sodium chromate.

In the above examples, in place of oxidizing agents such as sodium nitrate, other oxidizing agents have been employed with and without accelerating agents such as nitrates: For example, potassium persulphate and potassium permanganate.

Accelerating agents other than those mentioned in the above examples which have been employed are: manganese nitrate, cadmium nitrate, zinc nitrate, aluminum nitrate, chromium nitrate, barium nitrate, cobalt nitrate, nickel nitrate, lead nitrate, magnesium nitrate, and ferric nitrate.

In the following examples unless otherwise specified, aluminum articles were immersed in a 200 cc. solution at boiling temperature for 5 minutes.

*Example 20.*—One-half gram chromic acid, 3 cc. hydrofluosilicic acid were used to obtain a hard, medium gray uniform coating. The same solution was used except that 2 grams sodium nitrate were added. A brown coating was obtained, somewhat thinner and softer than the previous coating.

*Example 21.*—One-half gram chromic acid, with 2 cc. sulphuric acid were employed. A white, thin, fairly hard oxide coating was obtained. This was true also when 2 grams sodium nitrate were used with the other ingredients.

In place of the acids mentioned above which were used with chromic acid, nitric, hydrochloric, phosphoric, molybdic, tungstic, sulphurous and chloric acid were employed.

In the following examples similar conditions were employed in a 200 cc. boiling solution with the processing time 5 minutes, in each case employing aluminum objects. In this series of examples mineral acid salts are used to replace all or part of the mineral acids:

*Example 22.*—One-half gram chromic acid, 5 grams manganese silicofluoride was added to the solution and a medium hard coating was obtained. When the same ingredients are used with 2 grams sodium nitrate a harder, lighter, thinner coating is obtained.

*Example 23.*—One-half gram chromic acid, 5 grams sodium silicofluoride with 2 grams sodium nitrate. A hard, thin, light gray coating was obtained.

*Example 24.*—One-half gram chromic acid, 5 grams manganese sulphate with 2 grams sodium nitrate. A shiny, thin, hard gray coating is obtained.

*Example 25.*—One-half gram chromic acid plus 5 grams sodium molybdate with 2 grams sodium nitrate. A thin, shiny brown coating is obtained.

In place of the above salts there was used sodium sulphate, manganese chloride, sodium chloride, manganese nitrate, manganese dihydrogen phosphate, sodium dihydrogen-phosphate, sodium tungstate, potassium chlorate.

In the following examples under the same conditions chromium salts are used instead of chromic acid on aluminum surfaces:

*Example 26.*—2 grams potassium bichromate, 5 cc. sulphuric acid with 2 grams sodium nitrate. A very thin, white oxide coating is obtained.

*Example 27.*—2 grams potassium bichromate, 5 cc. hydrofluosilicic acid. Rather a soft gray coating is obtained. With 2 grams sodium nitrate added a hard brown coating is obtained.

*Example 28.*—2 grams chromium sulphate plus 5 cc. sulphuric acid with sodium nitrate. A white, thin oxide coating is obtained.

*Example 29.*—2 grams chromium sulphate plus 5 cc. nitric acid with 2 grams sodium nitrate. A white oxide coating is obtained.

In the above examples, in place of the potassium bichromate, sodium chromate has been employed. In place of the acids, hydrochloric, sulphuric and molybdic have been used.

Conditions of operation, proportions, ingredients and other factors may be varied to a considerable extent without departing from the spirit of the invention as will be well understood by anyone versed in the art, the scope of which is to be limited only by the following claims.

It has been found that great acceleration has been gained through adding to the solutions a soluble salt of a metal below the respective metal being treated in the electromotive series. In the case of iron and steel a salt of a metal slightly above iron, such as cadmium, may be used.

In the above examples proportions of chemicals used are for 200 cc. volume and panels processed were of 2" x 4" size.

What I claim is:

1. A process which comprises subjecting a metallic surface composed principally of one of the group consisting of iron, steel and aluminum to the action of a heated solution containing a soluble hexavalent chromium compound and an oxidizing agent selected from the group consisting of permanganates, nitrates, and persulphates, and also containing one of the group consisting of the $SO_4$ radical, the Cl radical and the $NO_3$ radical, at least one ingredient being added in the form of acid, and treating the metallic surface until a visible protective paint holding coating is obtained thereon and thereafter coating such surface with one of the group consisting of paints, lacquers and enamels.

2. A method which comprises subjecting a metallic surface composed principally of one of the group consisting of iron, steel and aluminum to the action of a heated solution containing chromic acid, an oxidizing agent of the group consisting of permanganates, nitrates, and persulphates, said solution also containing one of the group consisting of the $SO_4$ radical, the Cl radical and the $NO_3$ radical, at least one ingredient being added to the bath in the form of acid

and continuing such treatment until a visible protective paint holding coating is obtained upon the metallic surface and thereafter coating the surface with one of the group consisting of paints, lacquers and enamels.

3. A process which comprises treating a metal having a surface of one of the group consisting of iron, steel, aluminum and their alloys, with a heated solution containing a soluble hexavalent chromium compound, nitric acid and a nitrate, at least one ingredient being added in the form of acid and continuing such treatment until a visible protective paint holding coating is obtained upon the surface of the metal and thereafter coating such surface with one of the group consisting of paint, lacquers and enamels.

4. A process which comprises treating a metal having a surface of one of the group consisting of iron, steel, aluminum and their alloys, with a heated solution containing a soluble hexavalent chromium compound, one of the group of hydrochloric acid and soluble salts thereof and an oxidizing agent of the group consisting of permanganates, nitrates, and persulphates and continuing such treatment until a visible protective paint holding coating is obtained on the metallic surface and thereafter coating such surface with one of the group consisting of paints, lacquers and enamels.

5. A process which comprises treating a metal having a surface of one of the group consisting of iron and steel and their alloys with a heated solution containing a soluble hexavalent chromium compound, the $SO_4$ radical and an oxidizing agent of the group consisting of permanganates, nitrates, and persulphates, at least one ingredient being added in the form of acid and continuing such treatment until a visible protective paint holding coating is obtained upon the metallic surface and thereafter coating said surface with one of the group consisting of paints, lacquers and enamels.

6. A process which comprises treating a metal having a surface of one of the group consisting of aluminum and its alloys, with a heated solution containing a soluble hexavalent chromium compound, the $SO_4$ radical and an oxidizing agent of the group consisting of permanganates, nitrates, and persulphates, at least one ingredient being added in the form of acid to obtain a visible protective paint holding coating upon the metallic surface and thereafter coating the surface with one of the group consisting of paints, lacquers and enamels.

7. A process which consists in treating metal having a ferrous surface with a solution containing as its chief coating chemicals chromic acid and another oxidizing agent and continuing such treatment until a visible protective paint holding coating is obtained upon the surface of the metal, and thereafter applying and drying upon said surface a finishing coat.

8. A process which consists in treating metal having a ferrous surface with a solution containing as its chief coating chemicals a compound of hexavalent chromium, a compound comprising an acid radical, and an oxidizing agent other than the hexavalent chromium, at least part of one of said ingredients being introduced in acid form, and continuing the treatment until a visible coating is produced on the surface of the metal.

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