UNITED STATES PATENT OFFICE

2,313,756

METHOD OF ELECTROPLATING MAGNESIUM

William S. Loose, Midland, Mich., assignor to The Dow Chemical Company, Midland, Mich., a corporation of Michigan

No Drawing. Application March 1, 1939, Serial No. 259,287

2 Claims. (Cl. 294—32)

The invention relates to methods of electroplating metals. It more particularly concerns an improved electroplating bath for electroplating metals and a method of producing electroplated metal coatings, particularly upon readily oxidizable metals such as aluminum, magnesium, zinc, and alloys thereof in which an aforesaid metal is a predominant constituent.

Aluminum, zinc, and their alloys are difficult, and magnesium and its alloys practically impossible, to electroplate with an aqueous electroplating bath because such metals are relatively high in the electromotive series and tend to enter solution or form oxide coatings while immersed in the bath, preventing the electrodeposited metal from properly adhering to the article being plated. Articles of magnesium and its alloys, for example, cannot be plated by known aqueous electroplating baths which are suitable for heavy metals because of the tendency for the magnesium of the article to readily dissolve in such baths and also because magnesium and its alloys spontaneously form an oxide coating when immersed in aqueous baths, if these be slightly alkaline. In acid plating baths the oxide does not form, but instead the metal continuously passes into solution during the immersion. As a result, no commercially useful electrodeposited coating can be obtained.

The principal object of the invention is to provide a method of producing electroplated coatings upon readily oxidizable metals. A particular object is to provide a method of electroplating magnesium and its alloys.

Other objects and advantages will become apparent as the description proceeds.

I have discovered that by first suitably etching the article of readily oxidizable metal to be plated and then subjecting it to the action of an aqueous solution containing the ions of the metal to be deposited, together with a soluble fluorine component, and applying a suitable potential to the article which is made the cathode, strongly adherent, apparently continuous metallic coatings are obtained. The invention, then, consists of the plating bath and method hereinafter fully described and particularly pointed out in the claims.

In carrying out the invention the article to be plated, which may be either cast or wrought material, is cleaned, if necessary, of adhering dirt, scale, oxide, or grease in conventional manner as by wire brushing and subsequent treatment in alkaline detergent solutions such as those of sodium carbonate and sodium phosphate, or organic degreasing solvents such as carbon tetrachloride.

After the article has been cleaned, it is then ready to be treated according to the first step in the process. In this the article is subjected to the action of an etchant so as to produce a slightly roughened or pitted surface which serves to hold in place the electroplated deposit to be subsequently produced. Apparently the effective etchants are those which act mainly on the grain boundaries of the metal crystals. Various methods may be employed to produce the necessary etch, as by immersing the article in a pickling bath containing an agent which dissolves the metal, together with an agent which tends to produce a protective coating upon the metal. The protective coating which forms during the treatment does not completely cover the metal, but instead permits the etching agent to act largely upon the uncovered portions (these presumably being the grain boundaries), producing a slight pitting effect. After the article has been so treated, it is then, if necessary, subjected to a further treatment to remove any coating which may have been deposited during the etching step. If desired, etching solutions may be used which produce an etch without leaving a protective coating which has to be removed, obviating the necessity for further treatment before electroplating. If the etching solution produces a protective coating, however, it is usually necessary to follow such etching treatment with another treatment in a fairly concentrated aqueous solution of chromic acid or similar agent to remove the film or protective coating produced.

The composition of the etching bath to use may be varied to suit the metal article to be treated. The following are illustrative examples of suitable etching solutions to employ:

Example 1—Etchant for magnesium, zinc and their alloys
A relatively dilute aqueous solution containing from about 0.1 to 2 per cent of hydrofluoric acid. Etch in the solution for 1 to 10 minutes at room temperature.

Example 2—Etchant for magnesium and its alloys
Etch for 0.5 to 3 minutes at room temperature in an aqueous solution containing 1 to 15 per cent of hydrofluoric acid with from 0.5 to 10 per cent of either hydrochloric acid, nitric acid, chromic acid, ortho-phosphoric acid, acetic acid, tartaric acid, sulphuric acid, or a soluble salt of these acids.
Example 3—Etchant for magnesium and its alloys

Etch for 30 minutes in a boiling 10 per cent aqueous solution of a soluble chromate salt such as sodium dichromate.

Example 4—Etchant for magnesium and its alloys

Etch for about 5 to 30 minutes at about 50°C in an aqueous solution containing 10 per cent of sodium dichromate and 2 per cent of mono-sodium acid phosphate, while electrolysing the article as anode using about 5-50 amps./sq. ft. anodising current.

The foregoing etching baths, when used with magnesium and its alloys, for example, produce a protective film, and it is necessary thereafter to subject the article to a further treatment to remove this film before the electroplating step, as by treatment in an aqueous solution of chromic acid containing approximately 20 per cent thereof by weight. Such removal is effected by immersing the article in the solution for 1 to 3 minutes, preferably at the boiling temperature.

Example 5—Etchant for magnesium, zinc and their alloys

Dissolve 1.5 pounds of sodium dichromate and 1.5 pints of 68 per cent nitric acid in water to make 1 gallon of solution. Etch in the solution for 1/2 to 2 minutes at room temperature.

Example 6—Etchant for magnesium, zinc and their alloys

Dissolve 1 pound of chromic acid and 0.9 pint of 68 per cent nitric acid in water to make 1 gallon of solution. Etch in the solution for 1/2 to 2 minutes at room temperature.

Somewhat superior electroplates upon articles of magnesium and its alloys result when prior to the etching treatment of the Examples 2 to 6, inclusive, above the articles are first subjected to the action of hydrofluoric acid alone as by incubation for 1/4 to 10 minutes in aqueous hydrofluoric acid containing from about 0.25 to 50 per cent of anhydrous hydrofluoric acid.

Example 7—Etchant for aluminium and its alloys

Mix together 3 pints of nitric acid (60 per cent by volume) and 1 pint of hydrofluoric acid (30 per cent by volume). Etch in the mixture for 1 to 3 minutes at room temperature.

Example 8—Etchant for zinc and its alloys

Etch in a 10 per cent aqueous hydrochloric acid solution at room temperature until gas bubbles (hydrogen) begin to be evolved, and then remove the article from the solution.

After having produced an etched surface upon the article and removed, if necessary, any adhering protective film resulting from the action of the etching bath, the article may be carefully rinsed, preferably first with hot water and then with cold, but not dried, and then while still wet subjected to the electroplating operation. In some instances, as when the article is made of extruded metal which may show markings of the die used in its making, when subsequently plated, the article is preferably first given an additional etching or treatment in hydrofluoric acid solution of from 10 to 50 per cent concentration. The electroplating operation is carried out subsequently by electrolysing the article as cathode in an aqueous solution containing a soluble salt of the metal to be deposited, together with a fluorine component.

For nickel plating, such baths may be simple or complex according to the selection of the compounds employed in preparing the bath. Simple baths may be obtained by dissolving nickel carbonate in aqueous hydrofluoric acid solution, preferably in proportion such as to form the compound NiF₂·HF. A suitable concentration of nickel and of fluorine in such a bath is about 9 and 7 grams per liter, respectively. By adding potassium hydroxide to the bath until the pH is raised to about 4 its throwing power is increased.

The use of boric acid in nickel plating baths is advantageous and is illustrated in the following bath: Dissolve from 10 to 60 grams of nickel sulphate, 10 to 40 grams of boric acid, and 30 to 200 grams of potassium fluoride in water to make 1 liter of solution. The preferred proportions per liter are: nickel sulphate—40 grams, boric acid—20 grams, and potassium fluoride—75 grams.

Ammonium fluoride may be used in place of, or together with, boric acid. For example, 40 grams per liter of nickel sulphate and from 10 to 60 grams per liter of ammonium fluoride (preferably 60 grams per liter) in aqueous solution makes a good nickel plating bath. If boric acid is added, then the proportions may be as follows: nickel sulphate—10 to 60 grams per liter, ammonium fluoride—10 to 100 grams per liter, and boric acid—10 to 40 grams per liter. Best results are obtained when the pH values of these baths are between about 5 and 5.5.

For nickel plating magnesium and its alloys in general, the more complex plating baths are preferred to the simpler ones, best results being obtained when the constituents of the bath are present in such proportions as could form complex fluo compounds. This is obtainable by using a soluble salt of the metal to be deposited and a complex fluo compound as by employing a soluble alkaline metal or ammonium fluoride and an acid which forms therewith a complex fluo compound or such a fluo compound itself as sodium fluoroborate, fluosilicate, etc., in the bath. The proportions and concentrations of such compounds in the plating baths may be varied, but in general the soluble fluo compound and the soluble fluoride together should preferably be present in stoichiometrical excess of the soluble compound of the metal to be deposited.

For example, for the above-mentioned nickel plating bath, from 4 to 20 grams of nickel metal (from a salt thereof), from 12 to 50 grams of fluorine (from the soluble fluoride), and from 10 to 40 grams of boric acid per liter of solution should be used. The preferred proportions are 6 to 12 grams of metal to be deposited, 20 to 30 grams of fluorine, and from 12 to 24 grams of boric acid per liter of solution. The pH of the plating bath may be between about 4 and 6.5, and preferably between 5 and 5.5, as above mentioned. This may be obtained by employing hydrofluoric acid in place of or in addition to the soluble fluoride used. If desired, some other acids, e.g. sulphuric acid, may be used to adjust the pH of the bath.

As a further and general guide to the effective relative proportions of the ingredients for the complex type of plating bath, reference may be had to the following equation illustrating its application to a nickel plating bath:

\[
\text{NiSO}_4 + 3\text{KF} + 2\text{H}_2\text{BO}_3 = \frac{\text{N}_2\text{O}_5 + \text{3BF}_3 + \text{K}_2\text{SO}_4 + 6\text{KO}_H}{\text{N}(\text{BF}_3)_2 + \text{K}_2\text{SO}_4 + 6\text{KO}_H}
\]
According to the foregoing equation, the relative proportions of nickel, fluorine and boric acid to satisfy the equation are 58.79, 152, and 128.6 grams, respectively, and these same proportions are generally satisfactory for use in the plating bath. Similar equations can be written for other metals of the nickel family, e.g. cobalt, and for other acids forming with a soluble fluoride other complex fluo salts, such as nickel fluosilphonate, nickel fluosilicate, etc. Similar proportions can be used when depositing a combination of metals, for example, an alloy of cobalt and nickel.

Also, instead of employing a soluble salt of the metal to be deposited, together with a soluble fluoride and an acid forming therewith a complex fluo acid, a complex fluo salt of the metal may be used, such as nickel borofluoride (Ni(BF₄)₂), nickel fluosilicate (Ni(SiF₆)), etc., the pH of the bath being adjusted, if necessary, by adding, for example, suitable amounts of hydrofluoric acid when the pH is too high or sodium hydroxide when the pH is too low.

The following are further illustrative examples of plating baths:

**Example 9**
A nickel plating bath: nickel sulphate (NiSO₄·6H₂O)—40 grams, boric acid (H₃BO₃)—20 grams, potassium fluoride (KF·2H₂O)—80 grams, dissolved in water to make 1 liter of solution. Add hydrofluoric acid in sufficient amount to reduce the pH to between 5 and 5.5.

**Example 10**
A nickel plating bath: nickel sulphate (NiSO₄·6H₂O)—60 grams, boric acid (H₃BO₃)—30 grams, ammonium fluoride (NH₄F)—70 grams, dissolved in water to make 1 liter of solution. Add hydrofluoric acid in sufficient amount to reduce the pH to between 5 and 5.5.

**Example 11**
A nickel plating bath: nickel carbonate (NiCO₃)—88 grams, hydrofluosilicic acid (H₄SiF₄·H₂O)—92 grams of 28 per cent aqueous solution, potassium fluoride (KF·2H₂O)—106 grams, dissolved in water to make 1 liter. Add hydrofluoric acid in sufficient amount to reduce the pH to about 5.

**Example 12**
A nickel alloy plating bath: nickel sulphate (NiSO₄·6H₂O)—30 grams, cobalt sulphate (CoSO₄·7H₂O)—10 grams, boric acid (H₃BO₃)—20 grams, potassium fluoride (KF·2H₂O)—50 grams, and ammonium fluoride (NH₄F)—20 grams, dissolved in water to make 1 liter. Add hydrofluoric acid in sufficient amount to reduce the pH to between 5 and 5.5.

The electroplating step is then carried out by immersing the article (preferably while still wet from the previous step) in the plating bath, the article preferably having been previously connected to the source of electroploating current before immersion. An anode of the metal to be deposited may be used. The temperature of the electroplating bath should be maintained below that at which the complex fluo acid therein, if any, tends to decompose. In the case of the fluoboric acid bath, good electroplates are obtained at the temperatures between about 20° C. and 65° C. or higher. Similar temperatures may be used with the other baths. The current density to employ varies somewhat with the bath composition. I have found that in general a current density of about 5 to 40 amperes per square foot produces good results, but other current densities may be used. The duration of the electrolysis depends, of course, upon the thickness of the coating to be produced. It usually requires 30 minutes or more to obtain satisfactory coverage. After the coating has been deposited to the desired thickness, the article is removed from the plating bath and then immediately washed in cold water to remove any of the liquid of the electroplating bath. After such washing, the article may be rinsed in hot water and then allowed to dry.

After producing a nickel or nickel alloy deposit, as described, other metals may then be electrolytically deposited, if desired, directly on the deposit in conventional manner. This is particularly advantageous in the case of articles of magnesium and its alloys which cannot be conventionally directly electroplated with other metals. For example, after depositing nickel on an article of magnesium, as described, cadmium, chromium, copper, zinc, silver, etc., can be deposited thereon in conventional manner.

Attention is directed to a continuing application Serial No. 411,697, filed September 20, 1941, in which there is claimed a plating bath described in the foregoing specification.

Other modes of applying the principle of my invention may be employed instead of those explained, change being made as regards the method herein disclosed, provided the steps or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

I therefore particularly point out and distinctly claim as my invention:

1. In a method of depositing an electroplate of a nickel group metal upon articles of magnesium and magnesium-base alloys, the steps which consist in subjecting the article to the action of an acidified aqueous etching solution containing a soluble chromate to produce a protective coating on the article, then subjecting the article to the action of a boiling aqueous solution of chromic acid, and then electrolyzing the article as cathode in an aqueous solution containing a soluble fluoride, an acid forming with the fluoride a complex fluo acid, and a soluble salt of the metal to be deposited.

2. In a method of depositing an electroplate upon articles of magnesium and magnesium-base alloys, the steps which consist in subjecting the article to the action of an aqueous solution containing from 5 to 20 per cent of sodium bichromate and from 5 to 50 per cent of nitric acid, and then to the action of a heated aqueous solution containing up to 10 per cent of chromic acid, and then electrolyzing the so-treated article as cathode in an aqueous solution containing a soluble nickel salt, an alkali metal fluoride, and boric acid, said solution having a pH value between about 4.5 and 5.5.

WILLIAM S. LOOSE.