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# UNITED STATES PATENT OFFICE

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## PROCESS FOR ELECTRODEPOSITION OF METAL

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This invention relates generally to the electrolytic deposition of metals and more particularly to a process for depositing metals of the iron group on articles composed of aluminum and its alloys.

One object of the invention is to provide a process by which firmly adherent and smooth coatings of metals of the iron group may be cheaply and easily deposited upon electrically conductive surfaces.

Another object is to provide a process of depositing smooth, soft coatings of iron on articles composed of aluminum and its alloys.

Another object is to provide a new and improved electrolyte which, in addition to performing the usual functions of an ordinary electrolyte, is capable of maintaining substantially constant its initial degree of acidity or hydrogen concentration and when suitably agitated, of effectively preventing adherence of gases to the surface to be coated.

Other objects, more or less ancillary to the above objects, will appear and be pointed out in the appended specification.

In electrolytically depositing iron and other metals of the iron group in which I have included iron, nickel and cobalt, I have discovered that many serious difficulties encountered heretofore, of which the more important are perhaps brittleness, pitting and lack of adherence of the deposited metal to the article upon which it is deposited, can be avoided. A preferred means of accomplishing this result and obtaining uniformly smooth, soft, ductile and adherent metallic coatings consists briefly in practicing a new and improved process of cleaning the article on which the metal is to be deposited and then electrolytically depositing the metal thereon from an electrolyte of novel composition.

Theoretically, in electroplating, the electric current liberates free acid when it deposits metal from the electrolyte and then immediately causes combination of the free acid with a corresponding amount of metal from a metal electrode thereby maintaining constant the original acidity or hydrogen concentration of the electrolyte. Practically, however, an excess of free acid tends to accumulate as the process of deposition proceeds and the increased acidity or hydrogen concentration of the electrolyte is visibly indicated by the collection on the article being coated of bubbles of gas which is mainly hydrogen.

Increased acidity or high hydrogen concentration in the electrolyte is harmful to the depcsited metal since, in addition to causing pitting by adhering in bubble form to the article being coated, hydrogen also causes brittleness and peeling of the deposited metal by reason of being absorbed by or occluded therein. It, therefore, is essential to the obtaining of soft, ductile, adherent deposits that all gases, and particularly hydrogen gas, be prevented from adhering to the article being coated and that the hydrogen concentration of the electrolyte be maintained substantially constant at its original concentration.

Accordingly my process is adapted to avoid these harmful conditions by controlling automatically the hydrogen concentration in the electrolyte within certain narrow limits and removing any adhering gases from the article being coated.

For purposes of describing my process so that those skilled in the art can practice it, I have elected to describe it more or less in detail in connection with the depostion of an iron coating on the interior surface of a cylinder composed of aluminum alloys. In doing so, however, I do not wish to be understood as limiting the scope of my invention to the details set forth.

The first step in my process of coating the inner surface of an aluminum alloy cylinder with iron is to cleanse thoroly the surface to be coated and to provide minute interstices therein into which the deposited metal can penetrate and find anchorage. I do this preferably as follows. The cylinder is immersed in a dilute solution of sodium hydroxide for several minutes during which time the inner surface is constantly rubbed with a soft swab. Foreign substances and oxide coatings are thus removed and the surface is etched or appreciably roughened. Apparently a substantial amount of such etching is conducive to good adherence of the

deposited metal to the cylinder. Following cleaning and etching, the alkali is neutralized by immersing the cylinder in a dilute solution of nitric acid, after which the resultant salts, etc., are removed by dipping the cylinder in a very dilute solution of nitric acid. The cleaned cylinder is next dipped in a weak solution of acetic acid and rinsed with water and is then ready to be coated. If it is not to be coated immediately it may be left immersed in the acetic acid solution where it will be protected from oxidation until transferred to the electrolyte.

I have found that solutions of the following strengths are satisfactory for the above purposes.

| | Per cent solution |
|---|---|
| Sodium hydroxide | 10 |
| First nitric acid | 20 |
| Second nitric acid | 1 |
| Acetic acid | 1 |

Obviously other suitable solutions may be substituted for these solutions and the strength of each solution may be altered without departing from the spirit of my invention. It is also permissible to dispense with one or more of these solutions provided only that the article is suitably cleaned and etched and then freed from all reacting solutions and their products.

The second step of the process is the preparation of the electrolyte. The calculated amount of ferrous sulfate to form a saturated solution is first dissolved in water. After complete solution, ammonium hydroxide is added until the solution becomes of a thick sludge or mud-like consistency due to the precipitation therein of iron hydroxides and probably basic iron compounds. The electrolyte may also be formed by adding to a saturated ferrous sulfate solution a sufficient amount of precipitated ferrous hydroxide. Ferrous chloride and other suitable iron salts may be employed instead of the ferrous sulfate above specified.

The third and final step in the process is the actual deposition of the iron on the cylinder. It is accomplished by rotatably suspending the cylinder in the electrolyte around an iron anode and constituting it the cathode or negative terminal of an electric circuit. With an electrolyte temperature of about 70° F., a current density of approximately .026 amperes per square decimeter at 2½ volts and a speed of rotation of 250 revolutions per minute, a coating of iron will form on the cylinder which in the course of about 3 hrs. will amount to about .004″ in thickness. Prolonged action or increased current density will result in a thicker coating. This coating is smooth, free from all pits or surface depression, is soft, ductile and firmly adherent to the cylinder. After a coating of the desired thickness has been deposited the cylinder is removed from the electrolyte and washed with water after which the plate may be finished to size as by grinding or otherwise.

It is obvious that the precipitated substances in the electrolyte will effectively remove adhering gases from the article being coated when either the electrolyte or the article is agitated. The process may, accordingly, be practiced by suitably stirring the electrolyte rather than by rotating or moving the article being coated. For instance, the nature of the article to be coated might make it impossible to rotate or otherwise agitate the article in the electrolyte. An example is the coating of the interior surfaces of the cylinders in a cylinder block casting of an internal combustion engine. There the electrolyte itself may be caused to flow along and in contact with the cylinder walls by employing a pump, by suitable liquid propelling vanes on a rotating anode and by various other means.

Altho the reactions involved in electroplating are complex, in general, I believe the reaction by which the automatic control of the acidity or the hydrogen concentration of the electrolyte is brought about are as follows: Passage of a current of electricity thru the electrolyte deposits iron on the cathode and liberates sulfuric acid. The excess acid, which is not neutralized by metallic iron from the anode, then reacts with the precipitated iron hydroxide which permeates the entire electrolyte and which is in a condition favorable to prompt reaction with an acid thus forming neutral ferrous sulfate. In this manner the original acidity or hydrogen concentration of the electrolyte is maintained substantially constant. As the use of the electrolyte is prolonged, it may, of course, become necessary to add fresh quantities of precipitated iron hydroxide at intervals to replace that used in controlling the acidity of the electrolyte.

Altho I have described my process in some detail, as practiced on one particular article, it will be understood by those skilled in the art as being merely illustrative and that many variations in the steps of the process may be made without departing from the scope of my invention. It is also to be understood that my improved process is broadly applicable to the deposition of other metals of the iron group as above defined, and also to the deposition of such metals on articles composed of electrically conductive substances other than aluminum and its alloys.

All these modifications are comprehended by my invention, the scope of which is defined by what is claimed.

What is claimed:

1. An electrolyte for electrolytically depositing iron composed of a ferrous sulfate solution containing precipitated iron hydroxide

in suspension and having a thick mud-like consistency.

2. An electrolyte for depositing metals of the iron group which is characterized by having an excess of a metallic hydroxide of a metal of the iron group permeating the entire electrolyte in an amount sufficient to prevent gases adhering to a moving cathode and also to automatically maintain the acidity of the electrolyte substantially constant.

3. An electrolyte for electrolytically depositing metals of the iron group, composed of a solution of a salt of the metal to be deposited and containing hydroxide of that metal in suspension and characterized by being of a thick mud-like consistency.

4. A process for forming a coating of iron on metallic articles which comprises suitably preparing the article to receive an electrolytic deposit of iron, bringing the article into contact with an electrolyte characterized by containing iron hydroxide in suspension in sufficient amount to form a solution of thick mud-like consistency, and passing an electric current through the electrolyte and to the said article during relative movement of the hydroxide and article.

5. A process for forming wear resisting coatings of iron on metallic articles which comprises preparing an electrolyte of mud-like consistency containing iron hydroxide in suspension, cleaning the surface of the article to be coated, placing the said article in the electrolyte, passing an electric current thru the electrolyte and to the said article, and causing a rubbing gas removing action of the said hydroxide against the surface to be coated while automatically maintaining substantially constant the acidity of the electrolyte.

6. A process for electrolytically depositing metals of the iron group on aluminum alloy articles which comprises cleaning and etching the article to be coated, providing an electrolyte of mud-like consistency carrying in suspension a hydroxide of the metal to be deposited, bringing the hydroxide and the said article into contact, and causing constant relative movement therebetween while passing a current of electricity thru the said electrolyte to said article and while maintaining substantially constant the acidity of the electrolyte.

7. A bath for the electro deposition of metals of the iron group of thick mud-like consistency comprising a salt of a metal of the iron group in solution, and a finely divided hydrate of a metal of the iron group in suspension therein.

8. An electrolyte for use in the electrolytic deposition of metals of the iron group, characterized by possessing a thick, mud-like consistency and containing a solution of a salt of the metal to be deposited.

9. The process of depositing metals of the iron group from an electrolyte on a suitable cathode which includes the step of causing gas-bubble-removing, wiping engagement of the deposited metal with a precipitated mud-like mass of a hydroxide of the iron group in the electrolyte during the deposition of metal on the cathode.

In testimony whereof I affix my signature.

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