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R. A. SCHAEFER

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METHOD OF COATING METAL ARTICLES

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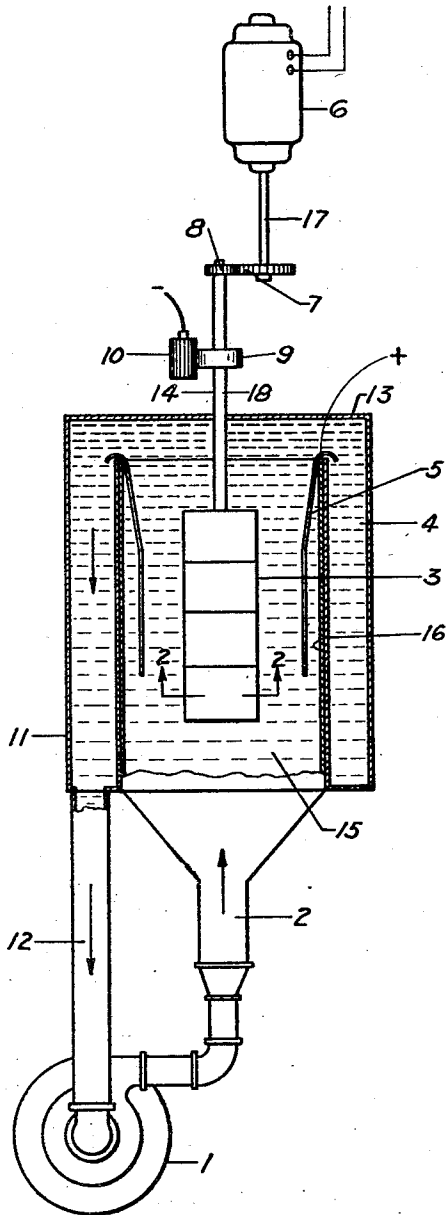


FIG. 1

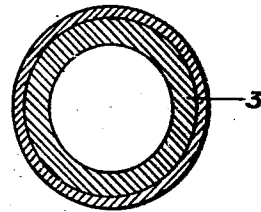


FIG. 2

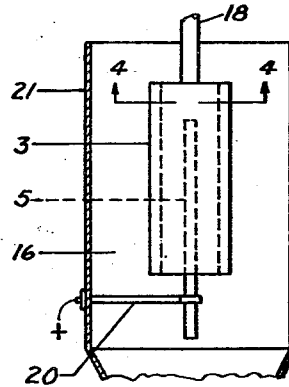


FIG. 3

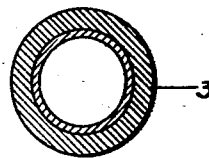


FIG. 4

INVENTOR.

Ralph A. Schaefer
Ray Macklin, Esq.
Williams, Chittam and Schaefer
ATTORNEYS.

BY

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METHOD OF COATING METAL ARTICLES

Ralph A. Schaefer, East Cleveland, Ohio, assignor to The Cleveland Graphite Bronze Company, Cleveland, Ohio, a corporation of Ohio

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7 Claims. (Cl. 204—40)

The present invention relates to an improved method of coating a metal article with a substantial layer of silver by electrodeposition. The primary object of the invention is to provide a method which produces a substantial layer of electrodeposited silver upon a metal base article at increased speed over present known methods and at the same time to provide a dense and ductile deposit.

Surface layers of silver have been successfully plated in the past but at a relatively slow rate of speed and in thicknesses usually of the order of less than .001 inch. When it was attempted to plate heavy layers of silver in the order of .020 to .030 inch the time required made it commercially impractical.

The present invention overcomes the difficulties encountered in the past by providing a method by which thick silver deposits can be obtained in relatively short periods of time. This is accomplished by means of relative movement between the solution and the article and also of the improved electrolytic bath which will presently be described, together with high current density.

It is a well known fundamental of electroplating that the rate of electrodeposition of metals is limited by the current density, the rate increasing with an increase in current density, provided the other factors be so chosen that a satisfactory result will be obtained. Thus, for instance, high current density plating without relative movement between the article surface and the electrolytic bath leads to a loose, non-adherent and porous plate. It is believed that the reason for this faulty plating is due to the depletion of metal ions in the vicinity of the cathode which causes an accumulation of gas at the cathode. In addition to these effects, polarization of the anode may lower the efficiency of the bath and slow down the process to such an extent that the original purpose is defeated and a defective plate may be produced.

Another factor disadvantageous to the use of high current densities is the tendency of the plated metal to build up in various regions in a dendritic pattern and thus present a rough, pebble-like surface which is very unsatisfactory. A further factor believed to inhibit electrodeposition of a desirable plate at high speed is the formation of a stagnant film on the cathode because of lower metal ion concentration.

Various means have been used to obtain relative movement between the article and the electrolytic bath in order to overcome the above objections, but it is still difficult to obtain a ductile, pore-free surface with the conventional electrolytic bath used for silver plating when relatively thick coatings are desired, since conventional baths at high current density give a brittle porous silver plate and the adhesion to a metal base will not withstand repeated stresses in the article.

One of the objects of the present invention is, therefore, an improved method of coating metal articles with silver by electrodeposition at an increased speed through the use of high current density. Another object of the invention is to provide a bath of a composition which will result in a ductile, pore-free and adherent coating of silver to a metal base. A further object of the invention is the adjustment of the relative movement between the article and the electrolytic bath and of the temperature in a way that they will all contribute in the article being plated by an adherent silver coating at a high speed.

To the accomplishment of the foregoing and related ends, said invention, then, consists of the means hereinafter fully described and particularly pointed out in the claims.

The annexed drawing and the following description set forth in detail one approved method of carrying out the invention, such disclosed method, however, constituting but one of the various ways in which the principle of the invention may be used.

In said annexed drawing—

Fig. 1 is a diagrammatic view illustrating a form of apparatus adapted to perform the process embodying the invention;

Fig. 2 is a sectional view taken along the plane 2—2 as shown in Fig. 1 and shows a typical plated article with the silver coating on the outside;

Fig. 3 is a part of a modified apparatus; and Fig. 4 is a sectional view similar to Fig. 2 with a coating on the inside of the article.

The apparatus illustrated in Fig. 1 is particularly applicable for the plating of the outside of cylindrical members with a relatively heavy coating of silver.

This apparatus comprises a chamber 4, which may be made of steel or any convenient material, and is enclosed by side walls 11 and a top 13; a rack 14 that serves for accommodating the article 3 which is to be silver plated and forms the cathode of the system. The anode, designated by the reference numeral 5, consists of silver rods which are suspended from the sides of a tank 16 and are connected to the positive line of a direct current supply (not shown). The upper part of the tank 16 is enclosed in chamber 4, while

the lower part is connected by a cylindrical portion 2 of reduced cross-section to the delivery side of a centrifugal pump 1 which keeps the electrolyte 15 in circulation as indicated by the arrows in the diagram. After having passed through the tank 16, the electrolyte is returned through chamber 4 and a pipe 12 to pump. This circulation of the electrolyte keeps the electrolyte uniform and aids in preventing metal depletion in the vicinity of the cathode thus preventing the formation of gas. It also aids in reducing the thickness of the stagnant cathode film and in keeping a high concentration of metal next to the cathode.

A motor 6 serves as a power source for rotating the rack 14 and thereby the cathode forming article 3. The driving connection is made by means of gears 7 and 8, mounted on shafts 17 and 18 respectively. The latter shaft also carries a commutator 9 contacting a brush 10, which element serves for establishing an electric connection between the cathode 3 and the negative line of the direct current supply.

The modified form of apparatus shown in Fig. 3 illustrates the device as adapted for coating the inside of the article. In this case the anode 5, consisting of a silver rod, is arranged within the cathode 3 on a bracket 20 attached to the side wall 21 of tank 16. All the other parts of the apparatus remain unchanged.

It is very essential in electroplating metals of any kind to provide the base metal in as clean a condition as possible and for that reason the articles before being placed in the assembly as shown, go through the following baths which are familiar to the art:

1. Solvent degreasing
2. Alkali degreasing
3. Acid pickle.

Acid pickle has the further advantage of etching the base metal so as to promote good bonding between the electrodeposited silver and the base metal.

The previously given steps clean the base metal sufficiently. However, when the article to be electroplated is rinsed in water after a pickle, which is the usual procedure of the art, a slight amount of oxidation takes place at the surface and prevents adhesion in certain areas. In cases of alloyed steels, this condition is augmented or diminished by different steels.

In order to prevent this oxidation I use a bath which contains a nickel salt, preferably nickel chloride, in high concentration, and acidify it slightly with hydrochloric acid. The bath temperature is preferably held at 85 to 100° C. The work is taken from the pickle tank when wet with acid solution and then rinsed in a dilute solution of acid, after which it is placed in the tank containing the nickel salt before the acid solution has time to dry. A dense coat of nickel is formed on the article which can be rinsed freely with water because the nickel covers the base metal and is more resistant to corrosion than the latter.

The nickel plating is followed by application of a silver strike which in turn is followed by the deposition of the silver surface layer.

For applying the silver strike a bath comparatively poor in silver cyanide and rich in alkali cyanide should be used. A particularly good bath for the silver strike consists of 2 grams per liter of silver cyanide and 40 grams per liter of potassium cyanide, the strike being applied from a source of current with a line potential of 6 to 8

volts and at a current density of 40 to 150 amperes per square foot. It is necessary to have the current on when the work is submerged in the bath to prevent formation of an immersion plate. This latter precaution is necessary to insure proper bonding of the silver to the article being electroplated, since an immersion plate has very poor bond and therefore serves as a poor base for a subsequent thicker layer of silver applied at high speed.

From the silver strike bath the article is transferred directly to the high speed plating apparatus, as shown in Fig. 1 or 3, while still wet with silver strike solution and with the current on before the rack is immersed in the electrolyte to prevent immersion plating in this stage of the plating as well. It is desirable for purposes of good bond between the silver and the base metal to have the solution moving and the work rotating when contact between them is made. Since the standard plating baths were found to be unsatisfactory for applying thick coats of silver to metal base articles, baths are used according to the invention having a composition which lies within the following limits:

	Grams per liter
Silver cyanide.....	30-70
Potassium cyanide.....	30-75
Potassium carbonate.....	40-100
Potassium hydroxide.....	5-30

The current density should not be too high, because with very high current densities, it is difficult to obtain a smooth adherent deposit, but it has been found that with the above plating bath a current density of 75-200 amperes per square foot with the circulation of the electrolyte previously described gives satisfactory results. As bath temperatures I found 40° to 80° C. to give very good results, but the process is, of course, not limited to these temperatures. The speed of rotation of the cathode is rather critical because if rotated too fast in plating the outer surface it throws the solution away from the work by centrifugal action and if rotated too slowly the solution rotates with the cathode and does not fulfill the necessary conditions for electroplating. Under the conditions cited above a rotation speed of about 80 R. P. M. for a 3" diameter tube has proved satisfactory. If the tubes are rotated too rapidly, then the plating surface is interfered with since the solution will cling to the surface to be plated forming a stagnant film on the cathode.

A silver bath which has given particularly satisfactory coatings consists of:

	Grams per liter
Silver cyanide.....	40-45
Potassium cyanide.....	35-40
Potassium carbonate.....	40-50
Potassium hydroxide.....	10-14

The potassium salts may be replaced in whole or in part by the same sodium salts. It is not known exactly what part the alkali hydroxide plays in the solution, but it is believed that it acts upon the anodes, performs a corrosive action with the aid of the electric current which in turn prevents polarization which is usually encountered in high speed plating. Another step which is highly desirable consists in filtering the solution at regular intervals to keep solid material out of the bath, which if present tends to give a rough plate or to cause metal trees to grow on the plate. At the temperatures given above for the operation of the silver plating bath the cy-

nide radical is continually decomposing giving off ammonia gas as an end product which must be removed from the electrolyte by aeration.

Any part of the article which it is desired to keep free of plate may be suitably masked by the use of rubber or various types of organic coatings which are commercially available.

With the apparatus and solution as described, it has been found that a smooth, pore-free layer of silver can be deposited in thicknesses of .010 to .020 inch per hour which is a materially greater rate than can be accomplished with any known method now available. Thicknesses up to .250 inch may be easily plated by this process.

Another method which has proven quite satisfactory for plating thick deposits of silver upon a base metal with the improved electrolytic bath as described consists in holding the article as a cathode in a stationary position and circulating the solution past it, thus obtaining the desirable feature of relative movement between the article and the electrolytic bath. This method is especially advantageous where it is desired to plate the inside of small diameter tubes since the clearance between the anode and cathode is small and rotation of the cathode might result in shorting between the anode and cathode due to improper alignment.

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

I claim:

1. A method of producing a thick non-porous silver plate by electrodeposition on a metal article which comprises pre-treating the article by plating with a thin layer of nickel and a silver strike mounting said article for rotation as a cathode and circulating an electrolyte over said cathode while rotating the same, said electrolyte consisting of per liter 40 to 50 grams silver cyanide, 35 to 40 grams potassium cyanide, 40 to 50 grams potassium carbonate and 10 to 14 grams potassium hydroxide, the current density being 75 to 200 amperes per square foot.

2. A method of producing a thick non-porous silver plate in the thicknesses of 0.010 to 0.020 inch per hour by electrodeposition on a metal article which comprises pre-treating the article by plating with a thin layer of nickel and a silver strike mounting said article for rotation as a cathode and circulating an electrolyte over said cathode while rotating the same, said electrolyte consisting of per liter 40 to 50 grams silver cyanide, 35 to 40 grams potassium cyanide, 40 to 50 grams potassium carbonate and 10 to 14 grams potassium hydroxide, the current density being 75 to 200 amperes per square foot.

3. A method of producing a thick non-porous silver plate up to 0.250 inch by electrodeposition

on a metal article which comprises pre-treating the article by plating with a thin layer of nickel and a silver strike mounting said article for rotation as a cathode and circulating an electrolyte over said cathode while rotating the same, said electrolyte consisting of per liter 40 to 50 grams silver cyanide, 35 to 40 grams potassium cyanide, 40 to 50 grams potassium carbonate and 10 to 14 grams potassium hydroxide, the current density being 75 to 200 amperes per square foot.

4. A method of producing a thick non-porous silver plate by electrodeposition on a metal article which comprises pre-treating the article by plating with a thin layer of nickel and a silver strike mounting said article for rotation as a cathode and circulating an electrolyte over said cathode while rotating the same at a rate of 80 rotations per minute, said electrolyte consisting of per liter 40 to 50 grams of silver cyanide, 35 to 40 grams of potassium cyanide, 40 to 50 grams of potassium carbonate and 10 to 14 grams of potassium hydroxide, the current density being 75 to 200 amperes per square foot.

5. A method of producing a thick non-porous silver plate by electrodeposition on a metal article which comprises pre-treating the article by plating with a thin layer of nickel and a silver strike mounting said article for rotation as a cathode and circulating an electrolyte over said cathode while rotating the same, said electrolyte consisting of per liter of 40 to 50 grams silver cyanide, 35 to 40 grams potassium cyanide, 40 to 50 grams potassium carbonate and 10 to 14 grams potassium hydroxide, the temperature of the bath being held at about 40 to 60° C., the current density being 75 to 200 amperes per square foot.

6. A method of producing a thick non-porous silver plate by electrodeposition on a metal article which comprises pre-treating the article by plating with a thin layer of nickel and a silver strike mounting said article for rotation as a cathode and circulating an electrolyte over said cathode while rotating the same, said electrolyte consisting of per liter 40 to 50 grams of silver cyanide, 35 to 40 grams of potassium cyanide, 40 to 50 grams of potassium carbonate and 10 to 14 grams of potassium hydroxide, the current density being 75 to 200 amperes per square foot.

7. A process for silver plating of a metal article which comprises pretreating the article by plating with a thin layer of nickel and a silver strike mounting said article as a cathode, immersing the article in an electrolyte consisting of 30-70 grams per liter of silver cyanide, 30 to 70 grams per liter of alkali cyanide, 40 to 80 grams per liter of alkali carbonate and 5 to 30 grams of alkali hydroxide and causing relative movement between the article and the electrolyte, the current density being 75 to 200 amperes per square foot.

RALPH A. SCHAEFER.