July 18, 1950 A. E. CHESTER 2,515,192

METHOD OF ELECTROPLATING

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Fig. 1

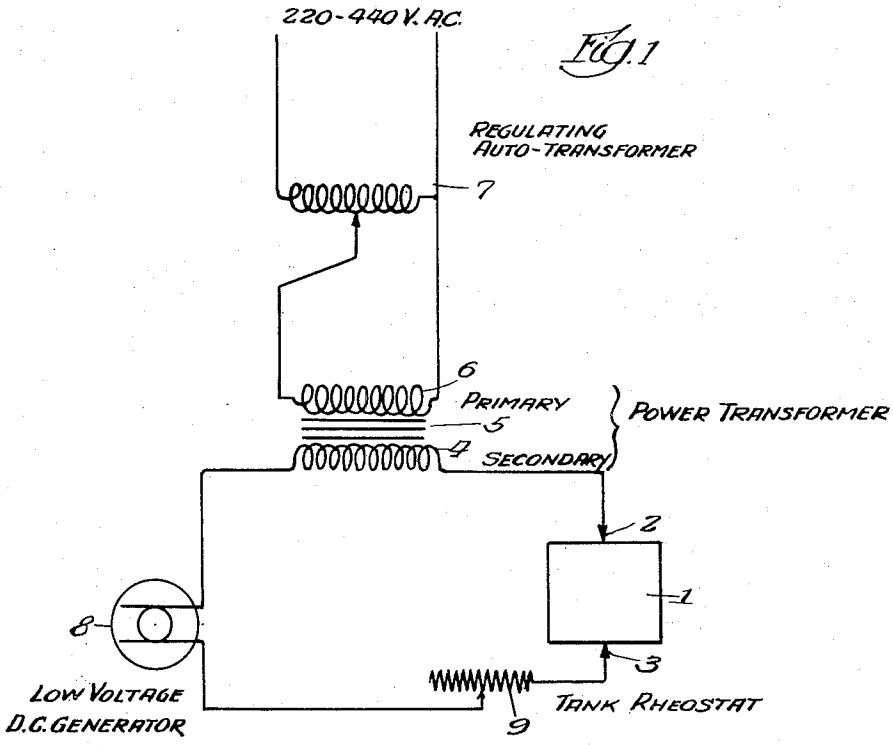


Fig. 2

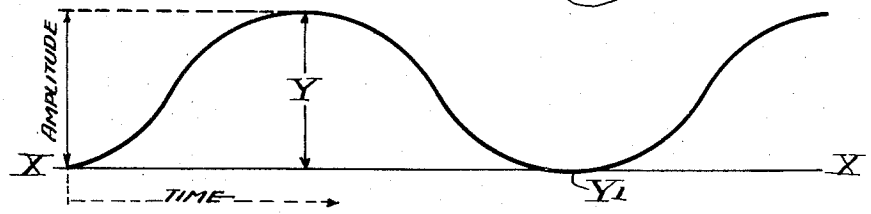
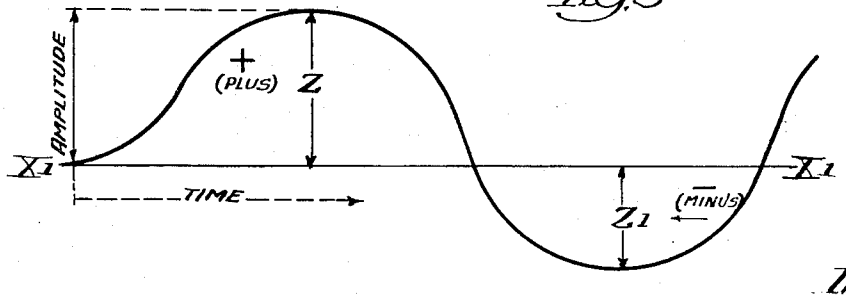


Fig. 3



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METHOD OF ELECTROPLATING

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2 Claims. (Cl. 204—45)

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This invention relates to a new and improved method of electroplating, and more particularly to a method of electrodepositing metals from a plating bath in a new and improved manner adapted to produce substantially uniform distribution on articles or objects of configurations such that the ordinary type of electroplating causes uneven distribution of the electrodeposited metal.

It is well known that flat objects, when electroplated in the usual way in an electroplating bath, tend to build up a higher concentration of metal near the edges than in the middle. This is true to some extent in objects of other configurations and various devices have been proposed in order to overcome this difficulty.

One of the objects of the present invention is to provide a new and improved method for overcoming the difficulty mentioned above and for electrodepositing metals from plating baths in a uniform manner.

Another object of the invention is to provide a new and improved method for electrodepositing metals on flat sheets or other flat objects in a manner such that substantial uniformity of distribution is obtained.

A still further object is the provision of a new and improved method for controlling the distribution of a metal from a plating bath.

Other features and advantages of the invention will appear hereinafter by reference to the following description thereof, in conjunction with the accompanying drawings in which

Fig. 1 illustrates diagrammatically one form of apparatus suitable for the practice of the invention;

Fig. 2 illustrates graphically one of the limits of the wave form of the plating current; and

Fig. 3 illustrates another limit of the wave form of the plating current in accordance with the preferred practice of the invention.

Generally stated, the invention involves a new and improved method of controlling the distribution of metal deposited on an electrically conducting surface from a plating bath by superimposing alternating current on direct current within certain predetermined limits. The invention is especially applicable to electroplating operations in which the work or article is so shaped that the electrodeposited metal builds up in some areas more than others. The plating current for the purpose of this invention may be described as an asymmetric alternating current in which the negative peak value of the wave form varies from zero (as illustrated in Fig. 2) to $-2/3$ of the positive peak value (as illustrated in Fig. 3).

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Referring to Fig. 1, the apparatus illustrated comprises a suitable receptacle 1 containing the plating bath, provided with one or more electrodes, generally indicated at 2, and a work piece or conducting surface to be plated, generally indicated at 3. As will be understood, the electrode 2 forms the anode and the work piece 3 the cathode.

The anode 2 is connected by suitable conductors to the secondary 4 of a power transformer having a core 5 and a primary 6. The primary 6 is connected to a regulating autotransformer, generally illustrated at 7, which in turn is connected to a suitable source of electrical energy, such as a 220 or 440 volt alternating current. Direct current is supplied by means of a low voltage current generator, generally shown at 8, one side of which passes to the work piece 3 through a rheostat 9, and the other side of which is connected to the secondary 4 in the manner shown.

In Figs. 2 and 3 the wave form of the current is graphically illustrated in a conventional manner, the horizontal axis (X—X) representing time and the vertical axis amplitude. The peak values are calculated from the equation

$$E=1.414\sqrt{E^2A.C.(R.M.S.)+E^2D.C.}$$

where E is voltage. For the wave form to be asymmetric, the negative peak value must drop below the X-axis. Thus, the wave form of Fig. 2 becomes asymmetric when the negative peak (Y_1) falls below the X-axis and is a different value from the positive peak value (Y in Fig. 2, Z in Fig. 3). Fig. 3 represents the maximum negative value (Z_1) which may be employed for the purpose of this invention. Any wave form similar to Fig. 2 in which the negative peak value is positive or above the X-axis may be described as pulsating direct current.

In a broader sense, the apparatus described and the hook-up of the component parts is believed to represent a new and improved system for the electrodeposition of metals by the superimposition of an alternating current on a direct current, irrespective of whether the ratios of alternating current to direct current are within the limits preferred for uniform distribution. Thus, this type of apparatus may be employed in plating articles of any configuration with other ratios of alternating current to direct current where the distribution of the electrodeposited metal is not

an important factor. This type of apparatus is suitable, therefore, for electroplating operations by the superimposition of alternating current on direct current in such a manner as to form a pulsating direct current.

The method of controlling distribution of the electrodeposited metal as described herein is especially suited for the formation of very thin, substantially uniform films or coatings of a metal on an electrically conductive surface. For example, it has been found that this invention is especially adapted for forming coatings of antimony on steel or cast iron objects in which the thickness of the coating is within the range of .000005 inch to .00005 inch. Steel or cast iron objects, when plated with antimony in accordance with the invention to the thickness described, are especially suitable for the addition of coatings of vitreous enamels, as described and claimed in my copending application Serial No. 555,953 filed of even date herewith. The thickness and uniformity of the plate is an important factor because it has been found that if the electrodeposited plate is insufficient, the desired bonding action will not occur. The same is true if the thickness of the coating is too great. Thus, this invention makes possible new and improved results in the art of enameling, as well as new and improved results in controlling the distribution of metals by electrodeposition.

The invention will be further illustrated but is not limited by the following examples, in which the quantities are stated in parts by weight unless otherwise indicated:

Example I

In 1 gallon of commercial 18° Bé. hydrochloric acid there were dissolved

6 ounces of antimony trioxide (Sb_2O_3)
2 ounces of arsenic trioxide (As_2O_3)
½ ounce of metallic selenium, and $\frac{1}{10}$%, based on the total weight of the mixture, of lauryl sulfate.

The resultant mixture is an acid electrolyte or plating bath suitable for the deposition of antimony on steel or other conducting surfaces in accordance with the invention, thereby to produce a ground coat to which the vitreous enamel is applied. The article to be plated, e. g., an article made of a conventional type steel, is immersed in the foregoing electrolyte as the cathode and is subjected to a superimposed asymmetric alternating current obtained by an electrical hook-up of the type described with reference to Fig. 1. The electroplating operation is preferably effected by superimposing a voltage of 3.2 A. C. (Root Mean Square) and 2.5 volts D. C. with a current density of 10 amperes per square foot for 8 to 15 seconds, or sufficient to produce a deposit on the order of 2 mgs. per square foot.

In the preparation of the antimony electroplating bath, the metallic selenium is added as a reducing agent. Other examples of suitable reducing agents are dissociable sulphur compounds such as ferric sulphide, poly sulphides, and other metals of the oxygen group of elements, such as tellurium.

The lauryl sulfate is employed as a surface active agent in order to enhance the smoothness of deposit, which otherwise would be affected by fine dirt particles. Its use is not absolutely necessary but is desirable and preferable, in accordance with the practice of the invention. As will be understood, other acid stable wetting agents may be used in an acid type of electroplating bath. Any suitably resistant type of anode may be used, such as for example a carbon anode. The type of electroplating bath just described may be described as a chloride bath, and represents a preferred type of bath for the practice of the invention.

Example II

The plating bath may be the same as in Example I with the omission of the reducing agent (metallic selenium), the surface tension reducing agent (lauryl sulfate), and/or the arsenic trioxide, although the results are less desirable for some purposes.

Example III

In the procedure described in Example I, an alkaline plating bath may be used instead of the acid bath, in which case a steel anode is employed, preferably made of cold rolled steel.

A typical composition for an alkaline bath is the following:

4.4 ounces potassium carbonate
2.11 ounces antimony sulphide (Sb_2S_3)

in one quart of water boiled for one hour and then filtered, the water lost by evaporation being replaced.

With an alkaline bath of this type the ratio of alternating current to direct current may be varied from that described in Example I in order to obtain the optimum plating conditions and to retain a wave form within the preferred range previously described, as indicated by the minimum and maximum limits of Figs. 2 and 3.

Example IV

Instead of the antimony plating bath, an arsenic plating bath may be used having the following composition:

1¾ ounces sodium arsenate
0.8 ounce 98% potassium cyanide
1 quart of water.

These are boiled together for ½ hour, then filtered and used at a temperature of 167° to 176° F. The ratios of alternating to direct current may be varied in order to obtain the optimum wave form in the manner previously described.

It will be understood that the invention is susceptible to some variation and modification in the manner of its practical application. Other metals than those described in the examples may be electrodeposited in accordance with the invention, including for example zinc, cadmium, tin, copper, bismuth, cerium, lanthanum, thorium, nickel, cobalt, and manganese.

As will be understood, antimony, arsenic and bismuth are metals in Group V B of the Periodic Table (Webster's New International Dictionary 2nd Edition Unabridged, 1941, vol. 2, page 1821); zinc and cadmium are in Group II B; copper in Group I B; tin in Group IV B; cerium and lanthanum are rare earth metals in Group III; manganese is in Group VII A, and cobalt and nickel in Group VIII.

The plating bath may be either an alkaline or an acid type, as for example, an alkaline zinc-cyanide bath, or an acid zinc bath, or an alkaline cyanide-cadmium plating bath, or an acid copper plating bath, or a cyanide-copper plating bath, or an alkaline tin plating bath.

The ratios of alternating to direct current which are preferably employed in accordance with the invention in order to obtain the desired

wave form, are about 2–4 volts (Root Mean Square) A. C.: 2.5 volts D. C., preferably at current densities from 2 to 15 amperes per square foot. Alternating currents of different frequencies may be used, but it is preferable to employ either a 25 cycle or a 60 cycle current. The plating time will vary depending upon the amount of metal which it is desired to deposit. Thus, for thicknesses of the type previously mentioned for vitreous enamel work, a plating time from 8 seconds to 1½ minutes is sufficient. It will be understood that higher current densities may be used, and that the alternating and direct current voltages may be larger or smaller, provided that the ratio produces a predetermined wave form of the type previously described. Thus, if the direct current is 0.5 volt, the alternating current would be correspondingly reduced in accordance with the foregoing ratio. If the direct current is 10 volts, the alternating current is increased in the foregoing ratio.

The plating current will be governed by the surface area of the article being plated, the size of the bath, power facilities and other factors which will be recognized by those skilled in the art.

The expression "antimony trichloride" plating bath is intended to include plating baths of the type described in Example I where other metals or salts thereof are present in minor proportion as well as those in which such metals or salts are absent.

The invention provides a new and improved method for controlling the deposition of metals on electrically conducting surfaces. It is especially useful in applying even, uniform coatings to articles having a configuration in which, by ordinary direct current plating methods, the deposited metal tends to build up in some areas more than others. Thus, it is especially important for electroplating flat surfaces when a thin plate of substantially uniform thickness is desired.

The invention is hereby claimed as follows:

1. In a method of controlling the electrodeposition of antimony from an antimony trichloride plating bath onto an electrically conducting object of a type in which the antimony would normally be deposited in greater concentrations in some areas than in others by a direct plating current; the step which comprises electrodepositing the antimony from an antimony trichloride plating bath by subjecting said object as a cathode in the plating bath to a plating current having an asymmetric alternating wave form comprising an alternating current superimposed on a direct current in the ratio of 2–4 volts R. M. S. to 2.5 volts D. C., regardless of the specific current values, at current densities from about 2 to about 15 amperes per square foot.

2. In a method of controlling the electrodeposition of metals from a plating bath onto a work piece of a type in which such metals are normally deposited in greater concentrations in some areas of the work than in others by direct current plating; the step which comprises electrodepositing antimony on said work piece as a cathode from an antimony trichloride plating bath by a superimposed alternating-direct plating current comprising an alternating current to direct current ratio from about 2 to about 4 volts R. M. S. alternating current having a frequency within the limits from about 25 cycles to about 60 cycles to about 2.5 volts D. C., regardless of the specific current values, at current densities from about 2 to about 15 amperes per square foot for a period of time within the range from 8 seconds to about 1½ minutes.

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