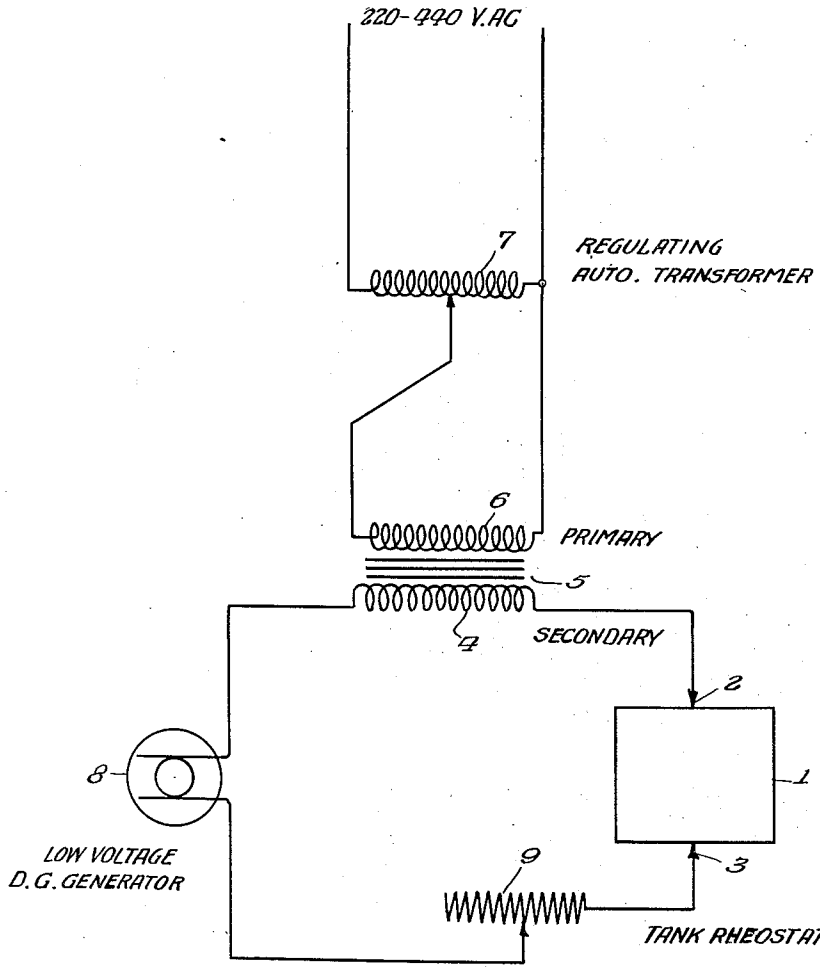
April 17, 1951 A. E. CHESTER 2,548,867

ELECTROPLATING METALS

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FIG. 1



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ELECTROPLATING METALS

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FIG. 2

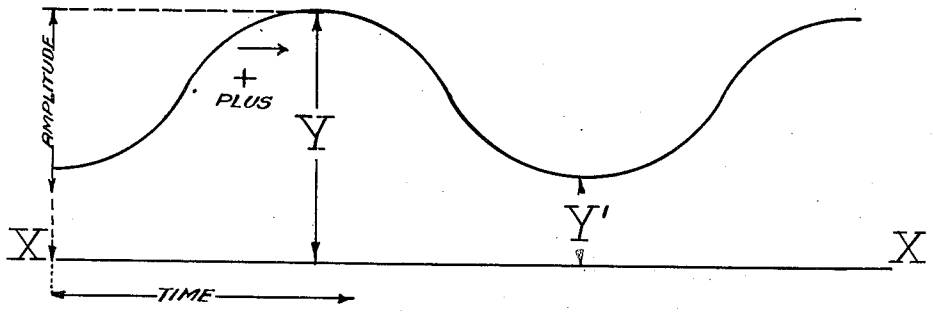


FIG. 3

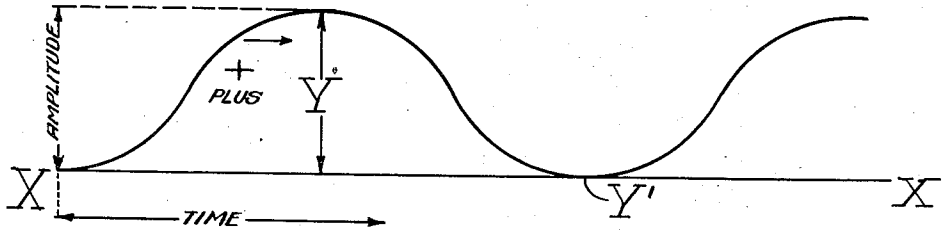
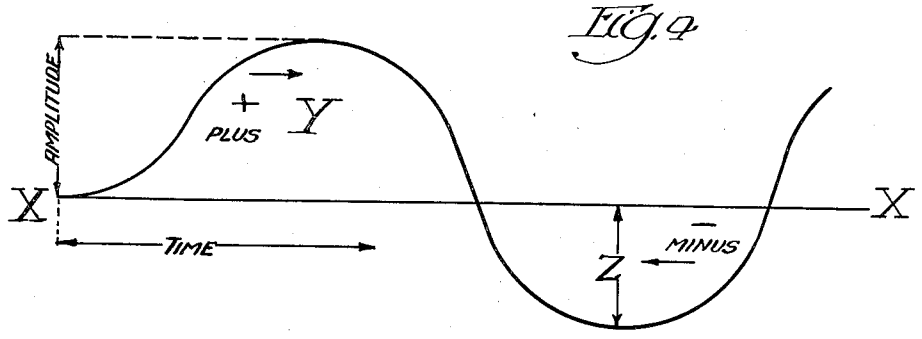


FIG. 4



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UNITED STATES PATENT OFFICE

2,548,867

ELECTROPLATING METALS

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Application April 14, 1945, Serial No. 588,399

5 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 electroplating metals from a plating bath in a new and improved manner adapted to increase the range of current densities over which bright deposits of metal can be obtained.

It is well known that bright deposits of metals from plating baths cannot be obtained at all with certain types of metals unless addition agents are added. In other cases bright deposits are obtained within certain narrow ranges of current densities. In these latter cases the use of higher current densities will produce dull or burned deposits of the metal. The use of higher current densities is desirable, however, to increase operating efficiency by increasing the speed with which the metal is deposited.

One of the objects of this invention is to provide a new and improved method for electrodepositing metals from suitable plating baths which, in the case of certain metals, will produce bright deposits without addition agents.

A further object of the invention is to provide a method of electrodepositing metals which will increase the range of current densities over which bright deposits can be obtained, as demonstrated on a Hull cell plate.

An additional object of the invention is to provide a method of electrodepositing metals from a plating bath containing brightening agents which will increase the range of current densities over which bright deposits can be obtained.

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

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

Figure 2 illustrates graphically one of the limits of the wave form of the plating current;

Figure 3 illustrates graphically an intermediate type of wave form of the plating current which may be used in the practice of the invention; and,

Figure 4 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 the use of abnormal wave forms in the plating current to produce new and improved results in the electrodeposition of metals from certain types of plating bath, more particularly, alkaline baths. The plating current for the purposes of this invention may be described as a plating current having an abnormal wave form characterized by peaks and valleys in which the valley voltage is within the range of a positive value of about 1.9 volts to a negative value which is not more than minus two-thirds of the positive value. The approximate maximum and minimum values are

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illustrated by the sinusoidal wave form shown in Figures 3 and 4 which illustrate asymmetric wave forms in which the valley voltages are from 0 volts to a minimum of minus two-thirds of the positive peak value. The invention, however, in its broader aspects is not limited to a sine wave form. Within this predetermined range the preferred valley voltage will vary with different types of plating baths, as more fully hereinafter described.

The abnormal wave form is preferably produced by superimposing an alternating current on a direct current.

Referring to Figure 1, the apparatus illustrated comprises a suitable receptacle 1 containing the plating bath, provided with one or more electrodes generally illustrated at 2, and a work piece or conducting surface to be plated generally indicated at 3. As will be understood, the electrode 2 forms an 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 Figures 2, 3 and 4 the wave form of the current is graphically illustrated in a conventional manner, the horizontal axis (X—X) represents time and the vertical axis amplitude. In practice the peak values and the valley values of the wave form are obtained by inspection from an oscilloscope (Coolidge tube) placed in the line between the anode 2 and the cathode or work piece 3.

The peak values and the valley values can be calculated theoretically by integral calculus. A method of calculation which gives values that are sufficiently accurate for practical purposes (say ±10% of the observed values) is as follows:

The peak values are calculated from the equation

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

where E is voltage.

The valley voltage is calculated by subtracting the D. C. value from the maximum value (E, as calculated above), multiplying the difference by the factor 2.0 and subtracting the product from the maximum value. This gives a valley, or negative voltage value in relation to the zero axis, which approximates the actual value, as observed on an oscilloscope.

The following is an example of this calculation:

D. C. value=6 A. C. value=7

(1) $6\times6=36$
$7\times7=49$
85

(2) Square root of 85=9.22—

(3) $9.22\times1.414=13.04$ maximum value

(4) $(13.04-6)\times2=14.08$
$13.04-14.08=-1.04$

In the wave form shown in Figure 2 the ratio of A. C. to D. C. current is such that the peak voltage Y and the valley voltage Y' are both positive. The resultant current, therefore, is pulsating direct current.

In the wave form shown in Figure 3 the peak voltage Y is positive and the valley voltage Y' is on the X—X axis. If the ratio of A. C. to D. C. current is such that the valley voltage Y' is negative, then the wave form becomes asymmetric, as illustrated in Figure 4. In Figure 4 the negative peak Z is a different value from the positive peak value Y and represents the maximum negative value which may be employed for the purpose of this invention. As previously indicated, this minimum value is such that Z is preferably not less than minus two-thirds of Y.

In practicing the invention it has been found that these abnormal wave forms produce new and improved results in the electrodeposition of metals from alkaline baths. The nature of the improvement may vary somewhat depending upon the type of metal deposited and the type of bath from which it is deposited. No marked improvement has been noted in acid baths containing no addition agents.

The invention will be illustrated but is not limited by the following examples in which the quantities are stated in parts by weight and the apparatus of Figure 1 is used, unless otherwise indicated.

Example I

A plating bath is prepared by adding

39 grams cadmium oxide
131 grams of sodium cyanide

to enough water to make a liter of plating bath. No addition agents are added. This bath is placed in the container 1 described in Figure 1 and a suitable work piece is suspended in the bath, as illustrated by the numeral 3.

This bath at room temperature with a working cathode density of 15–20 amperes per square foot has a cathode current efficiency of 85–98%. It exhibits no observable bright plating range with direct current alone when no addition agents are added to the bath.

When the bath is placed in the container 1 of the hookup shown in Figure 1 and subjected to a superimposed pulsating direct current in sine wave form consisting of 4 A. C. (R. M. S.) to 6 volts D. C., bright deposits are obtained within a current density range from about 10 to about 40 amperes per square foot. The valley voltage Y' is approximately +1.9. This example illustrates, therefore, that in an alkaline cyanide cadmium plating bath, the use of abnormal wave forms alone is sufficient to produce bright deposits, whereas such deposits cannot be obtained in an ordinary direct current bath without addition agents. Furthermore, if brightening agents are added to the bath the abnormal wave form will increase the range of current densities over which bright deposits can be obtained.

An extension in the bright range is obtained by using a ratio of A. C. to D. C. of 6 (R. M. S.) to 7 volts D. C., which gives a calculated valley voltage of +.96.

Example II

A copper plating bath is made up as follows:

15 ounces copper cyanide
15 ounces sodium cyanide
4 ounces sodium hydroxide
1 ounce potassium gluconate
1 gallon of water

The ingredients should preferably be thoroughly dissolved in the water using the heating coils in the tank to secure easier solution. After all of the ingredients are in solution, the bath should be filtered until it is perfectly clear.

Copper anodes are used and the anode-cathode ratio should be 2:1 or higher. Anode efficiency is about 100% under usual operating conditions, and an anode current density of from 8–20 amperes per square foot is preferred for best results. Care should be exercised that wetting agents are not carried into the electrolyte from the cleaner or pickling bath, as organic additions of this type will cause lack of adherence of the deposit and will also result in poor color and burning. Sulfur compounds of any type will produce pitting.

The operating temperature is preferably maintained at 175–185 degrees F. The cathode current densities are preferably 50–70 amperes per square foot. Cathode agitation should be employed because of the high rate of deposit and the resulting danger of concentrated polarization.

The bath may be purified in the conventional manner. Carbonates will form rather rapidly but are not harmful up to 65 grams per liter. In excess of that amount, they may be removed by barium or calcium hydroxide, or by other suitable means.

This bath will not produce satisfactory deposits when direct current alone is used as the plating current. Excellent results are obtained in the hook-up of Figure 1, however, with abnormal wave forms of the asymmetric type intermediate between those shown in Figure 3 and Figure 4, a preferred A. C. value being 7 and a preferred D. C. value being 6. The valley voltage is approximately —1.0. It will be understood that other current values may be employed in the same ratio to give comparable results.

The following table gives these ratios at the power source:

A. C. Volts	D. C. Volts
1.6	1.37
2.0	1.71
2.4	2.05
2.8	2.39
4.0	3.42
4.4	3.77
4.8	4.11
5.0	4.28
6.0	5.14
7.0	6.00

In this case, also, bright deposits are obtained solely by the use of abnormal wave forms. If desired, potassium gluconate may be omitted from the bath.

The electrolyte analysis of this bath during

electroplating operations is preferably controlled within the following range:

	grams/liter	ounces/gallon
Copper (as metal)	65–95	8.7 –12.7
Free Cyanide	3– 8	0.4 – 1.08
Caustic Soda	25–32	3.35– 4.3
pH Colorimetric	10.8	

Example III

A plating bath is prepared from the following ingredients:

75 grams of sodium cyanide
45 grams of zinc oxide
15 grams of sodium hydroxide

and enough water to make a liter of solution. Good results are obtained in plating from this bath with a ratio of A. C. to D. C. of 1.6 (R. M. S.) to 4 volts D. C. This current ratio gives a pulsating direct type of current in which the wave form is intermediate between that described in Figure 2 and that described in Figure 3. The valley voltage is approximately +1.9.

Example IV

A plating bath is prepared from the following ingredients:

90 grams of sodium stannate
7.5 grams of caustic soda
15 grams of sodium acetate
0.5 gram of hydrogen peroxide or sodium perborate

and sufficient water to make a liter of solution.

This bath gives a smooth white tin deposit at temperatures of 60–80 degrees C. and current densities of 15–30 amperes per square foot, which is not bright over any range of current densities when direct current alone is used.

With a preferred superimposed current of A. C. to D. C. in the ratio of 1:1 bright deposits are obtained within the range of 20–40 amperes per square foot. The calculated valley voltage is approximately —0.0006. The anode current efficiency which is around 60–70% on quadrivalent tin with direct current is between 70 and 90% with the superimposed A. C. to D. C. current.

Example V

The method described in Example III is carried out with the addition of $\frac{1}{10}$ of 1% by weight (i. e., 1 gram per liter) of lauryl sulfate and 10 grams per liter of calcium gluconate. The lauryl sulfate acts as a surface tension reducing agent. It may be omitted, if desired. The calcium gluconate serves to control the carbonate content of the solution.

The principles given in the foregoing description and examples may be employed with good results in plating other metals from alkaline plating baths. Especially good results have been obtained in plating metals from alkaline cyanide baths. If organic addition agents are employed in the bath to increase the brightness of the deposits, the use of abnormal wave forms, as herein described, will extend the bright range, or the range of current densities over which bright deposits can be obtained. It is, therefore, possible in the practice of the invention to obtain bright deposits of a predetermined thickness in a shorter period of time as compared with previously known methods.

The use of abnormal wave forms in accordance with the invention also makes it possible to employ higher current densities with less burning.

Good results have been obtained in the practice of the invention with alternating currents having frequencies of 25 cycles to 60 cycles, inclusive. The upper frequency limits can be determined by experiment with any given plating bath by carrying out the invention with varying frequencies and noting the point at which an improvement in the brightening effect is no longer obtained.

This application is a continuation-in-part of my co-pending application, Serial No. 441,694, filed May 4, 1942, which has now become U. S. Patent No. 2,443,599.

Having thus described the invention, what I claim and desire to secure by Letters Patent of the United States, is:

1. A method of electrodepositing bright plates of metals from alkaline baths which comprises passing a plating electric current including direct and alternating current components of abnormal asymmetric sine wave form having peaks and valleys through an alkaline plating bath of a metal from the group consisting of zinc, cadmium, copper and tin, the valley voltage of the wave form being from 0 volts to a minimum of minus two-thirds of the positive peak value, and the alternating current component having a frequency within the limits from about 25 cycles to about 60 cycles.

2. A method of electrodepositing bright zinc which comprises passing a plating electric current including direct and alternating current components of asymmetric sine wave form having peaks and valleys through an alkaline cyanide-zinc plating bath, the valley voltage of the wave form being from 0 volts to a minimum of minus two-thirds of the positive peak value, and the alternating current component having a frequency within the limits from about 25 cycles to about 60 cycles.

3. A method of electrodepositing bright cadmium which comprises passing a plating electric current including direct and alternating current components of asymmetric sine wave form having peaks and valleys through an alkaline cyanide-cadmium plating bath, the valley voltage of the wave form being from 0 volts to a minimum of minus two-thirds of the positive peak value, and the alternating current component having a frequency within the limits from about 25 cycles to about 60 cycles.

4. A method of electrodepositing bright copper which comprises passing a plating electric current including direct and alternating current components of asymmetric sine wave form having peaks and valleys through an alkaline cyanide-copper plating bath, the valley voltage of the wave form being from 0 volts to a minimum of minus two-thirds of the positive peak value, and the alternating current component having a frequency within the limits from about 25 cycles to about 60 cycles.

5. A method of electrodepositing bright tin which comprises passing a plating electric current including direct and alternating current components of asymmetric sine wave form having peaks and valleys through an alkaline tin plating bath, the valley voltage of the wave form being from 0 volts to a minimum of minus two-thirds of the

positive peak value, and the alternating current component having a frequency within the limits from about 25 cycles to about 60 cycles.

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