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PROCESS OF ELECTRODEPOSITING COPPER, SILVER, OR BRASS

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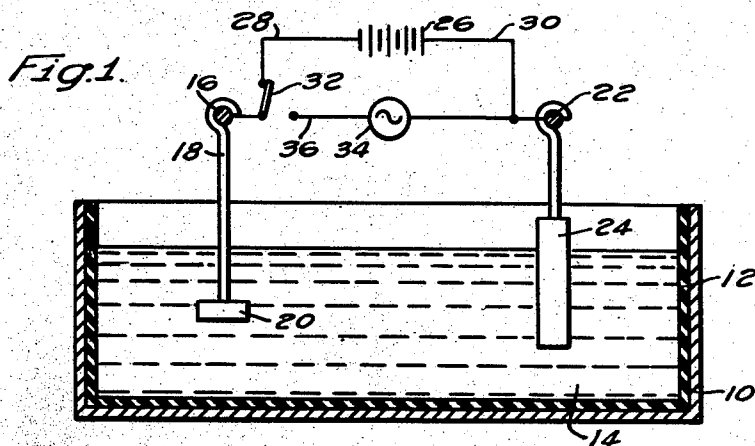
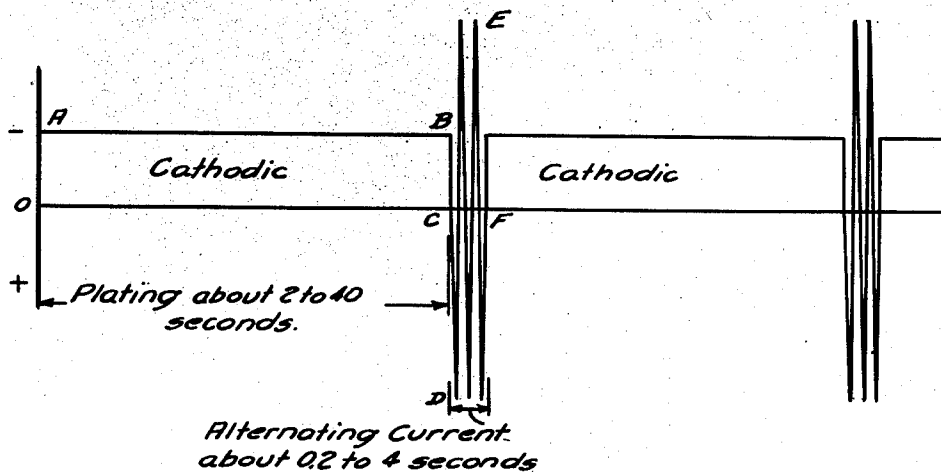


Fig. 2.



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PROCESS OF ELECTRODEPOSITING
COPPER, SILVER, OR BRASSGeorge W. Jernstedt, Belleville, N. J., assignor to
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This invention relates to electroplating and more particularly to a novel process of electroplating.

In electrodepositing metals on a base member from an electrolyte by using direct current alone in the conventional manner, there are definite limitations both as to the speed of plating and the obtainable quality of the electrodeposited metal. In particular, as thicker coatings of electrodeposited metal are produced unusually great care is required, since they tend to become progressively rougher and the quality rapidly deteriorates. Furthermore, in the electroplating upon base members having complex shapes, and especially such, for example, that have sharp projections, cavities, or recesses, or other non-uniformities, it is difficult to produce electrodeposited coatings of acceptable quality without resorting to time-consuming and costly expedients specific to each individual type of member to promote uniform plating. For these reasons, the electroplating of metals is a highly developed art requiring great skill to secure reasonably good coatings of metal on base members. Furthermore, electroplated metal almost invariably must be subjected to extensive after treatment to render it more acceptable. Buffing, polishing, grinding and other work is necessary to produce a satisfactory polish, brightness or smoothness for many purposes. This requires a great deal of hand labor and increases the cost of the plated articles considerably.

The present invention is directed to the application of a predetermined current cycle to the base member being plated whereby the electrodeposited metal is rendered sufficiently bright, smooth and uniform as plated so that not only is buffing, polishing or grinding eliminated, but more homogeneous metal is produced than possible with ordinary direct-current processes.

The object of this invention is to provide for depositing on a base member a sound and homogeneous electroplate.

A further object of this invention is to provide for electrodepositing on a base member metal by successive brief periods of direct current and intermittent periods of alternating current whereby superior plated metal is produced.

Other objects of the invention will, in part, be obvious and will, in part, appear hereinafter. For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description and drawing, in which:

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Figure 1 is a vertical cross-sectional view through a plating tank, and

Figure 2 is a graph of the current cycle of the present invention.

According to the present invention, metal is electrodeposited from an electrolyte upon a base member by applying consecutively and separately, first, a conventional direct current rendering the member cathodic to deposit an increment of metal from the electrolyte, followed by an alternating current alone at a much heavier current density for a brief interval to smooth out and otherwise improve the previously deposited thickness of increment of metal. Repetition of this cycle will build up the required electrodeposit. The base member may be of metal of any usual kind; thus it may be a casting, a forging, sheet metal, drawn wire or the like; or it may be a conducting non-metallic material such as graphite, coke, molybdenum disulfide, certain conducting refractories and the like.

Referring to Fig. 1 of the drawing, there is illustrated a suitable apparatus for carrying out the process of this invention. The electroplating tank 10 provided with a suitable chemically resistant resistance liner 12 carries an electrolyte 14 from which the metal is to be electrodeposited. A current conductor 16 carries a support 18 for a base member 20 which is immersed in electrolyte 14 for electrodeposition of metal thereon. A second conductor 22 supports a typical anode 24 which may be either of the same metal as being deposited on the base member 20 or may be of an inert material such as graphite, platinum or the like. A suitable source 26 of direct current such as a battery, a rectifier or a direct-current generator supplies current through a conductor 28 to the conductor 16 to render the base member 20 cathodic when the metal is to be plated thereon. The conductor 30 furnishes current to the anode 24. A switch 32 is provided for making and breaking the circuit between conductors 28 and 16, and to connect and disconnect an alternating-current generator 34, or other source of alternating current meeting the requirements of this invention, with the conductor 16. A conductor 36 from the generator 34 is disposed so that the switch 32 will bring it into circuit with the conductor 16 upon movement of the switch 32 to break the circuit from the direct-current source 26.

It will be apparent that the switch 32 is capable of being manipulated to connect alternately and separately the conductor 16 and base

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member 20 with the direct-current source 26 and the alternating-current generator 34. The switch 32 may be manually operated, but for practical purposes it is preferably operated by suitable timing mechanism, such, for example, as a cam driven by a synchronous motor geared down to a predetermined rate of movement to move the switch 32 between the conductors 28 and 36 at predetermined intervals. In other cases relays operated by timing mechanisms of various types may be employed. In some cases, a timed drum contact member having conducting and nonconducting areas may be employed to alternately connect the direct-current source and the alternating-current source to the base member in accordance with the requirements of the invention.

Exemplary of the current cycle applied to the base member 20 is a curve plotting current density against time as shown in Fig. 2 of the drawing. At the point O unidirectional direct current is applied to the base member to render it cathodic and the current density will reach a value A. The cathodic current is applied to the base member 20 for the interval from A to B which is preferably from about 2 to 40 seconds. In actual practice, it has been found that highly satisfactory results are obtained if the time between A and B is approximately 4 to 8 seconds. At time B, the circuit from the direct-current source is broken and the current density drops to approximately zero at C. It will be appreciated that while the current from A to B is shown as uniform direct current, this is not necessarily required. The current from A to B may be rippled or pulsating direct current, or may vary so that the value at A is much greater than the value at B. It should be mentioned, however, that for plating any given metal from any selected electrolyte, the average current density at A to B will be much higher than that which can be successfully used with constant direct current. Thus, for example, a current density of 100 amperes per square foot for A to B has been successfully employed in a cyanide copper bath when using the cycle of the present invention which is much higher than could be employed under the same conditions using regular direct current continuously. Such higher current densities have been applied in plating in accordance with this invention with good results.

At the point C, an alternating current fluctuating in polarity and current density from D to E is applied for a period of time of approximately one-tenth the period of time that the base member was cathodic in the previous direct-current portion of the cycle. Thus the alternating current is applied for about 0.2 to 4 seconds. Furthermore, it is desirable that the alternating current be such that at least one complete cycle is applied to the base member so that the base member is anodic and cathodic at least once.

The frequency of the alternating current may be varied within a wide range. The voltage and current density of the alternating current will vary somewhat with the frequency. With 60-cycle current, it has been found that for normal copper plating as well as other metal plating that is carried out at voltages of less than 10 volts using direct current only, the alternating current should have a value of at least 20 volts and preferably from 30 to 40 volts. Alternating current, of 60 cycles, at 110 volts has been employed, but the current density is quite high and no corresponding benefits are secured. An

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alternating current of about 30 volts is recommended since excellent results may be obtained and the current density is maintained at a peak of about 300 amperes per square foot. The alternating-current frequency may be as low as one cycle per second, or even lower, with good results. In silver plating, alternating-current frequencies of less than one cycle per second have been found advantageous in that they will give good results with current densities as low as 150 to 200 amperes per square foot.

The alternating current need not be of the usual sine wave shape, but may be of various other wave shapes. The alternating current, for example, may be produced by reversing a high potential source of direct current by a suitable timing mechanism at predetermined intervals to produce a series of roughly square waves. It is critical, however, that the voltage and current density of the alternating current be much higher than that of the direct-current portion of the cycle at A to B. In many cases, the alternating current preferably should terminate at F with the base member being anodic to secure the maximum smoothness and luster in the electroplated deposit.

The alternating current C, D, E, F may be superimposed on an anodic direct current with certain advantages. The anodic direct current may be of a current density of either more or less than the cathodic current density at A to B, but should not be so great that some substantial part of the peaks in the portion E is not cathodic. The superimposition of an anodic direct current and alternating current is beneficial in that deplating of the high spots and corners occurs to a greater extent than in the absence of the anodic current. If the anodic current is substantial, the time for the interval C to F may be reduced thereby reducing the overall plating time.

The exact nature of the reaction that takes place during the alternating-current portion of the cycle is not known. It is believed that the alternating current, due to its high potentials, reacts strongly during the anodic portions of the cycle at the elevated points to deplate from the high spots and rough projections a portion of the increment of electroplated metal produced during the previous interval between A to B. However, any low or unplated spots are not deplated in the same proportion as the burrs, corners, projections or elevations or other high spots. When the alternating current cycle is cathodic, the metal is replated, but appears to be redistributed more uniformly over the low and high spots. It will be understood, of course, that the main contours of the base member are not affected by the alternating current to the same extent as the microscopic projections consisting of burrs, cracks, scratches, pores and the like. It is definitely shown by examination of the electroplated member that there is a great increase in the smoothness and brightness of the metal coating deposited during the portion A to B after being subjected to the alternating-current portion of the current cycle. By repeating the cycle A to F there are obtained successive microscopically thin increments of highly satisfactory electrodeposited metal superimposed on one another. By suitable control of the time and current, an electrodeposit of any selected thickness may be built up. There will be little or no tendency to produce nodules, dendrites, pores, coarse crystals or other objectionable plat-

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ing defects. The final product is a bright plate which is of somewhat greater density, is harder and more corrosion resistant than conventional direct-current plating. In fact the plated metal surfaces have been much smoother than the original base metal.

Example 1

A typical example of the application of the invention is the plating of members in a Rochelle copper solution, for which the following Rochelle copper electrolyte was employed:

	Ounces per gallon
Copper cyanide	4
Sodium cyanide	5
Sodium carbonate	2
Rochelle salts	5

The electrolyte was maintained at a temperature of 160° F. The current cycle employed in this bath was 4 seconds at a direct-current density of 50 amperes per square foot and 0.3 second at 30 volts, 60-cycle alternating current at a current density of about 300 amperes per square foot. A very bright, lustrous and smooth coating was deposited on a steel base member. The copper deposit was so bright and smooth that it did not require any buffing or polishing. It was ready for use without any treatment other than drying.

Example 2

An electrolyte of the following composition for plating brass was employed:

	Grams per liter
Copper cyanide	30
Zinc cyanide	9.5
Sodium cyanide	56

The electrolyte was at a temperature of 100° F. when applied. The same current cycle was employed as in Example 1. A bright brass deposit was produced on steel plates. A bright brass electrodeposit has been regarded as highly desirable in the electroplating art, but hitherto has not been commercially possible by any known plating process. The bright plate produced by the practice of the present invention was very smooth and homogeneous. The base member with the brass plate was suitable for use at once.

Example 3

For silver plating, the following electrolyte was prepared:

	Grams per liter
Silver cyanide	40
Potassium cyanide	62
Free potassium cyanide	40
Potassium carbonate	50
Potassium hydroxide	10

The bath was maintained at room temperature. Silver was plated for a period of time applying a cycle comprising a plating direct current for a time of 8 seconds at a current density of 15 amperes per square foot then with alternating current applied for 0.8 of a second at a current density of 300 amperes per square foot using 60-cycle alternating current at 30 volts, and repeating this cycle. Excellent silver plate was secured. The silver plate was sufficiently bright so that no hand buffing or polishing was required.

Example 4

In another case silver plating was carried out with the above electrolyte using a cycle first applying a plating direct current at a current

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density of 75 amperes per square foot for 5 seconds, and then a 60-cycle alternating current at 300 amperes per square foot applied for 0.5 second. The temperature of the electrolyte was 175° C. The electrolyte was stirred vigorously. Excellent silver plate was secured.

It will be appreciated that alloys as well as single metals may be electrodeposited by the present alternating-current process. Likewise several successive deposits of metal in any desirable proportions may be plated on a single member.

A further advantage of the process is the easier plating of complex members to provide a relatively uniformly thick electrodeposit on all surfaces without the use of special anodes, thieves or other expedients. I have been able to plate both the inner and outer surfaces of a square casing approximately 6 inches on a side and 4 inches deep, both ends being open, using no internal anodes.

Electrodeposition of metals by alternately and intermittently applying alternating current in combination with direct current enables the plating process to be greatly expedited. Plating times can be reduced to 25% to 50% of the time required with direct current alone.

The electrolyte may be agitated or distributed in accordance with well known practices in plating. It has been found desirable to maintain a clean electrolyte, for example, by filtering or the like, since the electro-deposits have such a highly polished surface that any solid impurities from the electrolyte deposited on the plated work are much more apparent than in ordinary electroplating. The temperature of the electrolyte may be varied to suit the plating requirements. The current cycle works as well at temperatures of boiling water as at temperatures below room temperature.

The metal electrodeposited in accordance with the process herein disclosed has the properties and characteristics of the metal electrodeposited by the alternating or reverse current process set forth in my copending patent application Serial No. 610,107, filed Aug. 10, 1945, now Patent No. 2,451,341, granted October 12, 1948.

It is intended that all matter contained in the above description or in the accompanying drawing shall be taken as illustrative and not in a limiting sense.

I claim as my invention:

1. In the process of electrodepositing a metal from the group consisting of copper, silver and brass upon a base member from an electrolyte suitable for the electrodeposition of the metal, the steps comprising applying the electrolyte to the base member, passing a unidirectional electrical current at a voltage of not over 10 volts through the base member and the electrolyte to render the base member cathodic for a predetermined period of time of from about 2 to 40 seconds to electrodeposit metal upon the base member, terminating the cathodic current, passing an alternating current through the base member and electrolyte, for a shorter period of time of approximately 0.1 of the period of cathodic current, at least one complete cycle of alternating current being applied to the member in this period, the alternating current having a higher peak voltage than the cathodic voltage, and repeating applying the cathodic current and alternating current cycle until a desired thickness of metal has been electrodeposited on the base member.

2. In the process of electrodepositing a metal from the group consisting of copper, silver and brass upon a base member from an electrolyte suitable for the electrodeposition of the metal, the steps comprising applying the electrolyte to the base member, passing an electrical current through the base member and electrolyte at a potential of below 10 volts to render the base member cathodic for from about 2 to 40 seconds to electrodeposit metal on the base member, terminating the cathodic current, passing an alternating current through the base member and electrolyte at a potential of at least 20 volts for from about 0.2 to 4 seconds, and repeating the cathodic current and alternating current cycle until a desired thickness of metal has been electrodeposited on the base member.

3. In the process of electrodepositing a metal from the group consisting of copper, silver and brass upon a base member from an electrolyte suitable for the electrodeposition of the metal, the steps comprising applying the electrolyte to the base member, passing an electrical current through the base member and electrolyte at a potential of below 10 volts to render the base member cathodic for from about 2 to 40 seconds to electrodeposit metal on the base member, terminating the cathodic current, passing an alternating current through the base member and electrolyte at a potential of at least 20 volts for from about 0.2 to 4 seconds, at least one complete cycle of alternating current being applied during the time interval, and repeating the cathodic current and alternating current cycle until a desired thickness of metal has been electrodeposited on the base member.

4. In the process of electrodepositing a metal from the group consisting of copper, silver and brass upon a base member from an electrolyte suitable for the electrodeposition of the metal, the steps comprising applying the electrolyte to the base member, passing an electrical current through the base member and electrolyte at a potential of below 10 volts to render the base member cathodic for from about 2 to 40 seconds to electrodeposit metal on the base member, terminating the cathodic current, passing an alternating current through the base member and electrolyte at a potential of from at least 20 volts to 110 volts for from about 0.2 to 4 seconds, at least one complete cycle of alternating current being applied during the time interval, the alternating current being terminated during the anodic portion of the cycle, and repeating the cathodic current and alternating current cycle until a desired thickness of metal has been electrodeposited on the base member.

5. In the process of electrodepositing a bright and smooth coating of copper upon a base member the steps comprising applying to the base member an aqueous alkaline electrolyte containing copper cyanide, passing an electrical current at a voltage of not over 10 volts through the base member and electrolyte to render the base member cathodic for a period of from about 2 to 40 seconds to electrodeposit copper on the base member, terminating the cathodic current, passing an alternating current through the base member and electrolyte at a potential of at least 20 volts for from 0.2 to 4 seconds, at least one

complete cycle of alternating current being applied in the time interval, and repeating the cathodic current and alternating current cycle until a desired thickness of copper has been electrodeposited on the base member.

6. In the process of electrodepositing a bright and smooth coating of silver upon a base member the steps comprising applying to the base member an aqueous alkaline electrolyte containing silver cyanide, passing an electrical current at a voltage of not over 10 volts through the base member and electrolyte to render the base member cathodic for a period of from about 2 to 40 seconds to electrodeposit silver on the base member, terminating the cathodic current, passing an alternating current through the base member and electrolyte at a potential of at least 20 volts for from 0.2 to 4 seconds, at least one complete cycle of alternating current being applied in the time interval, and repeating the cathodic current and alternating current cycle until a desired thickness of silver has been electrodeposited on the base member.

7. In the process of electrodepositing a bright and smooth coating of brass upon a base member the steps comprising applying to the base member an aqueous alkaline electrolyte containing copper cyanide and zinc cyanide, passing an electrical current at a voltage of not over 10 volts through the base member and electrolyte to render the base member cathodic for a period of from about 2 to 40 seconds to electrodeposit brass on the base member, terminating the cathodic current, passing an alternating current through the base member and electrolyte at a potential of at least 20 volts for from 0.2 to 4 seconds, at least one complete cycle of alternating current being applied in the time interval, and repeating the cathodic current and alternating current cycle until a desired thickness of brass has been electrodeposited on the base member.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,431,047	Ruben	Oct. 3, 1922
1,534,709	Holt	Apr. 21, 1925
1,565,216	Smith	Dec. 8, 1925
1,566,265	Antisell	Dec. 22, 1925
1,712,284	Turnock	May 7, 1929
1,785,389	Piersol	Dec. 16, 1930
1,918,605	Jones	July 18, 1933
1,935,395	Engle	Nov. 14, 1933
2,063,760	Schulein	Dec. 8, 1936
2,181,773	Wernlund	Nov. 28, 1939
2,451,341	Jernstedt	Oct. 12, 1948

OTHER REFERENCES

"Modern Electroplating" (1942), page 173, published by American Electrochemical Society (an article by Benner et al.).

Transactions of the Faraday Society, vol. 24, No. 85, part 6, pages 348-358, June 1928.

Transactions of the American Electrochemical Society, vol. 41, (1922), pages 151-180.