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ELECTROPLATING

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This invention relates to the electrodeposition of iron, platinum, osmium, iridium, rhodium, palladium, ruthenium, lead and indium, and alloys thereof in which these metals form the predominant constituent, by means of a periodically reversed electrical current.

This application is a continuation-in-part of my copending application, Serial No. 610,107, filed August 10, 1945.

In electroplating metals upon base members, it is highly desirable to produce electrodeposits thereof that are as smooth as possible, and of maximum brightness. Furthermore, it is ordinarily desirable that the metal being deposited be applied upon a given base member in a relatively uniform thick coating. Heretofore, employing conventional continuous direct current for electroplating it was recognized that due to current concentration phenomena dependent upon the shape of the base member in conjunction with other factors, such as concentration of ions containing the metal to be plated in the body of the solution adjacent the base member, the electrodeposits ordinarily vary greatly in thickness from point to point on a base member. This unequal building-up of the electrodeposits on various portions of the member is not only inefficient due to excessive use of metal, but is in many cases undesirable because it leads to aggravated conditions such, for example, as treeing, nodules, extreme roughness and other inferior electrodeposits. In order to remove excessive electrodeposits which build up on corners and sharp edges and similar places where excessive current concentrations occur, considerable handwork consisting of buffing, grinding, polishing and the like has been required as a necessary step in producing commercially acceptable electrodeposits.

It is well known to those skilled in the art that many electrodeposits contain pores and other unplated flaws that extend to the base member. The protective value of the electrodeposits may be greatly diminished because of the presence of such unplated areas, since corrosion is most readily initiated at the pores and the like. It would be highly desirable to produce electrodeposits that substantially completely cover the base member without any appreciable number of pores or areas in which the electrodeposit is thinner than over the major portion of the plated member in order to secure optimum protective or decorative coatings.

As is further well known to those skilled in the art, the electrodeposition of metals by con-

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tinuous direct current must be carried out below certain current densities if a given degree of quality of plated work is to be secured. The plating current densities employed commercially are ordinarily maintained below certain maximum permissible limits in order that the plater have a safe margin within which to operate. Continuous direct current plating, therefore, requires an extensive amount of equipment since the amount of work that can be plated per unit time in a given plating tank is proportional to the allowable plating current density. Any increase in allowable current density that would result in the production of satisfactory plated work proportionately reduces the number or size of plating tanks, the amount of solution in use, and related apparatus that would be required.

In my copending patent application, Serial No. 610,107, filed August 10, 1945, of which the present application is a continuation-in-part, there is disclosed a method of electroplating metals from electrolytes containing such metals in solution by employing a periodically reversed electrical current. Periodically reversed electric current enables the electroplater to control and improve the entire plating operation with certain unexpected advantages accruing. It enables the electroplating process to be so carried out that one or more of the following advantages over continuous direct current plating are obtained:

- (1) Increase in the rate of plating,
- (2) Increase in the density of the metal deposited,
- (3) Improved brightness of electrodeposited metal surface,
- (4) Greater smoothness in the electrodeposited metal,
- (5) Heavier deposits are platable,
- (6) Decreased porosity, and
- (7) Improved electrodeposited metal distribution on base members.

The periodic reverse current process may be so applied to any particular plating electrolyte that any one feature of the above seven can be particularly emphasized. Therefore, it will be apparent that the periodic reverse current process gives the electroplater a means for controlling his plating process in a manner that is not available when employing only continuous direct current or other conventional current cycles disclosed in the prior art.

The object of the present invention is to provide for the electrodeposition of iron, indium, lead, the platinum metals and alloys in which

these metals predominate, by means of a periodically reversed electric current to enable improved plating to be obtained.

A further object of this invention is to enable the control of the electroplating process to secure predetermined electrodeposits by applying a selected periodically reversed current cycle.

Other objects of the invention will, in part, be obvious and will, in part, appear hereinafter.

It has been discovered that iron, lead, indium, platinum, osmium, iridium, rhodium, palladium, ruthenium and alloys in which these metals predominate, i. e. exceed 50% by weight, may be electrodeposited from electrolytes containing the metal in solution by applying thereto a periodically reversed current consisting of a series of successive cycles of which each cycle first delivers a plating electric current to render the base member being plated with the metal cathodic for a period of time of not more than 40 seconds to plate an increment of the metal thereon, and then applies a deplating electric current to render the base member anodic to deplate a portion of the previously plated increment. The cycle is repeated until a predetermined thickness of metal is built up on the base member. It is desirable that the deplating electric current which renders the base member anodic be of such a magnitude and be applied for such a period of time that it delivers to the base member from $\frac{1}{20}$ to $\frac{1}{2}$ the coulombs delivered during the preceding plating period. For most plating applications, the optimum results have been obtained when the deplating electric current has delivered to the base member from 15% to 40% of the coulombs delivered in the immediately preceding plating period.

In many cases the efficiency of the plating and deplating periods in this cycle approaches 100%, since polarization and other effects tending to reduce current efficiency do not occur to any appreciable extent and, therefore, the amount of metal plated is almost directly proportional to the coulombs applied during the plating period and the amount of metal deplated is likewise proportional to the number of coulombs delivered during the deplating period. However, the efficiency during either the plating or deplating portion of the current cycle may be less than 100%, but the periodic reverse current process will operate effectively at any degree of efficiency.

The most unexpected improved results have been obtained by employing the periodic reverse current cycle of this nature in electroplating the metals listed above. Fundamentally periodic reverse current enables a greater degree of control of the plating operation and type of plating produced. Electrodeposits of a quality similar to continuous direct current plating have been obtained when the current density was increased considerably over previously accepted maximum plating current density limits. However, the increase in speed of plating is not the most important result when employing periodic reverse current. The distribution of electrodeposited metal over the surface of a base member being plated may be so uniform and of such a degree of smoothness that the quality of the electrodeposit is outstanding.

In many cases, the surface smoothness of the electrodeposited metal produced in accordance with the practice of this invention has been such that it is far smoother than the original base metal surface. I have been able to plate a metal

coating of 0.0005 inch thick that was of a smoothness of from 1 to 4 micro-inches R. M. S. from edge to center of a rectangular panel, which panel to start with had a surface 10 micro-inches and rougher. As is well known to those skilled in the art, it is almost impossible to electrodeposit metal by continuous direct current that is as smooth as the original base member since the tendency during electrodeposition is to build up an electrodeposit that magnifies the roughness of the original base member. In many cases, by the practice of this invention, metals have been plated with an extremely bright surface and in most cases, plating can be conducted with every metal to produce a mirror-bright surface requiring no buffing, polishing, or other finishing operations at the completion of plating. Other advantages of the periodically reverse current cycle applied to the metals listed herein will be set forth hereinafter.

It is desirable that the plating electric current that renders the base member being plated cathodic whereby an increment of metal is plated thereon should not be applied for more than 40 seconds. The plating period of time may be as little as 0.01 of a second or even less. Since it is most convenient and practical to simply reverse the flow of the plating current from a constant current source at intervals by a suitable switching or current reversing mechanism whereby the base member is rendered anodic at the same current density at the cathodic current density so that a portion of the previously plated increment is deplated, the ratio of the times of plating period to the deplating period under these conditions will determine the ratio of coulombs of plating to deplating current. A variety of mechanisms is available to the trade that will permit plating current to flow in a circuit for a period of time from 40 seconds to 0.01 second or less, and then the flow of current is reversed so that the base member is rendered anodic for a period of time of 20 seconds or less, whereby the deplating current flows for a period of time of from $\frac{1}{2}$ to $\frac{1}{20}$ of the previous plating time. Suitable mechanism for this purpose may consist of relays, switches, rotating or sliding commutators, operated by timers and the like interposed in the circuit from a source of direct current, such, for example, as a generator, rectifier, batteries or the like. In some cases a hand operated reversing switch may be operated manually at timed intervals.

It has been found that in many cases further advantages accrue when the deplating current density is greater than the plating current density applied to a base member in the periodic reverse current cycle. As disclosed in my copending application, Serial No. 791,027, filed December 11, 1947, the current density during the deplating portion of the cycle may be greatly increased over the plating current density by introducing either an additional source of current or a resistance into the circuit.

In each cycle after an increment of metal has been plated, it has been found that due to the functioning of the plating apparatus the build-up of the metal on the base member is irregular and any corners, projections, high spots and the like tend to acquire electrodeposits of metal of a greater thickness than at low spots or within cavities or over areas that may have a resistant surface film. Upon reversing the flow of electrical current within 40 seconds, the reversed current deplates the metal and the deplating is concen-

trated at the very spots that the plated increment increased disproportionately. This effect is particularly pronounced with increased reverse current density but is sufficient even at the same or lesser current density so that when from $\frac{1}{2}$ to $\frac{1}{20}$ of coulombs of the amount applied during the previous plating current have been delivered, the projections and other unduly built up portions of the electrodeposit will be greatly reduced by a preferential deplating action and the low spots or the like may have little or no metal removed therefrom. On reversing the current again so that plating recurs in the next cycle, the low spots and the like tend to plate a greater thickness of metal than would be deposited if plating had not been interrupted by the deplating current. The net effect of a plurality of cycles of plating and deplating current is that smoother and more uniform electrodeposits are applied to the base member. In one instance a thickness of 0.001 of an inch of metal plated by periodic reverse current applied to a shot blasted steel surface completely concealed the original surface and the plated metal was extremely smooth.

The following examples are illustrative of the practice of the invention:

Example I

An aqueous solution of the following composition for iron plating was prepared:

	Ounces per gallon
Ferrous chloride	45
Manganese chloride	0.5

The pH of the solution was 0.7 and its temperature was 160° F. The addition of a slight amount of hydrochloric acid gives a desired pH. A base member was placed within the solution and the following electric current cycle was applied to the base member:

Cathodic	15 seconds at 20 a. s. f
Anodic	1.1 seconds at 34 a. s. f.

A smooth bright deposit of iron was produced. The plating could be continued for prolonged periods of time to produce extremely heavy thicknesses of iron plating such as is required in iron molds and the like without rough plated metal surfaces being encountered.

Example II

An iron plating solution was prepared by dissolving 375 grams of ferrous chloride in sufficient water to make one liter. The solution at a pH of 1.3 was maintained at a temperature of 155° F. Excellent iron plated deposits that were so smooth that they did not require buffing and were bright were produced by using the following plating cycles:

	Seconds
Plating	0.05
Deplating	0.01

and

	Seconds
Plating	2.5
Deplating	1.5

The current density could be varied up to over 100 amperes per square foot for plating and deplating in each of the cycles (a) and (b) with outstanding iron plating deposits being obtained.

Example III

An aqueous solution was prepared having dissolved therein:

	Grams per liter
Ferrous chloride	375
Manganese chloride	7.5

The pH of the solution was 1.3 and it was maintained at a temperature of 150° F. Smooth bright deposits of iron were plated from the solution at current densities of up to 100 amperes per square foot for both portions of the following cycles:

	Seconds
Plating	0.05
Deplating	0.01

and

	Seconds
Plating	5
Deplating	1

Example IV

A solution for iron plating was prepared with the following components:

	Grams per liter
Ferrous chloride	375
Ferrous sulfate	30
Manganese chloride	7.5

The pH of the solution was 1.3 and it was maintained at a temperature of 140° F. Iron electrodeposits that were smooth, bright and extremely uniform were produced at current densities of up to 100 amperes per square foot for the plating and deplating portions of the following cycles:

	Seconds
Plating	5
Deplating	1

and

	Seconds
Plating	0.05
Deplating	0.01

Example V

A solution for the plating of platinum was prepared by combining the following:

Disodium phosphate	grams	110
Ammonium hydroxide 28%	cc	15
Platinum salt (61% platinum)	grams	6.5
Water to make 1 liter.		

The electrolyte was maintained at 180° F. Smooth bright platinum deposits were plated upon base members by applying the following periodic reverse current:

10 seconds cathodic at 30 amperes per square foot,
and
3 seconds anodic at 22 amperes per square foot.

Example VI

An aqueous electrolyte for plating palladium was prepared of the following composition:

	Grams per liter
Palladium metal	2.5
Sodium hydroxide	7.5

The temperature of the electrolyte was 150° F. Palladium metal was deposited from the solution upon a base member by applying to the base member an electric current rendering the base member cathodic for 15 seconds at a current density of 33 amperes per square foot, and anodic

for 3.5 seconds at a current density of 30 amperes per square foot. Smooth deposits that were substantially better than those obtainable with continuous direct current were produced.

Example VII

An aqueous electrolyte for the plating of rhodium of the following composition was prepared:

Concentrated sulfuric acid.....cc. per liter...	20
Rhodium metal.....grams per liter...	2

The temperature of the electrolyte was 40° C. Platinum anodes were employed and the base member was plated by applying thereto a current to provide a density of 20 amperes per square foot of the base member, and the current was periodically reversed to deliver to the base member a plating current for 5 seconds and a deplating current for 1 second. In 7 minutes the base member was plated with approximately 0.00001 inch of smooth mirror-bright rhodium metal which would be suitable for mirrors and light reflector applications and the like.

Solutions of osmium, iridium and ruthenium may be prepared as in Example VII by substituting soluble salts of these metals for the rhodium and plating with periodic reverse current under the same conditions to secure deposits of these metals. Mixtures of two or more metals in a solution will enable alloys to be plated by applying thereto the periodic reverse current of this invention.

Example VIII

An aqueous electrolyte for lead plating was made up as follows:

	Grams per liter
Fluoboric acid 42%.....	320
Basic lead carbonate.....	135
Glue.....	3

This solution was operated at room temperature and smooth uniform deposits of lead were deposited on base members with the following reverse current cycle:

	Seconds at 30 a. s. f.
Cathodic.....	10
Anodic.....	2.5

Other lead electrolytes, such as the sulfamates, may be plated to advantage using periodic reverse current as here disclosed.

Example IX

Electrodeposits of indium may be plated from aqueous solutions containing 2 to 3 ounces of indium hydroxide per gallon and 10 to 12 ounces of tartaric acid per gallon mixed together and then made ammoniacal with ammonium hydroxide. In some cases one ounce of ammonium chloride per gallon of solution may be added to the electrolyte. Plating may be carried out at room temperature. The indium metal may be plated on a base member using a cycle whereby the base member is rendered cathodic for 1 second and anodic for $\frac{1}{2}$ second, at a current density of 30 amperes per square foot. Indium deposits of great smoothness and uniformity may be applied by this process on bearing shells and the like.

Example X

An aqueous electrolyte containing 7 ounces per gallon of ferrous sulfate and 7 ounces per gallon of nickel ammonium sulfate and 4 ounces per gallon of boric acid, at a pH of 2.8, at 140° F. was plated using a cycle of $\frac{1}{20}$ second plating current

and $\frac{1}{20}$ second deplating current both at a current density of 40 amperes per square foot. A smooth coating of iron nickel alloy having iron as the major constituent was deposited.

It will be appreciated that the electrolytes in the above examples are exemplary and not exhaustive. In general, it may be stated that any electrolyte from which the given metal may be plated by continuous direct current may have applied to it periodic reverse current in accordance with this invention and improved plating obtained.

The electrolytes may be agitated or stirred with advantage while plating with periodic reverse current. Since periodic reverse current produces such smooth bright plate, any contamination or dirt in the electrolyte is more evident on the plated work and, therefore, filtering, preferably continuously, is recommended to secure the best electrodeposits.

The preparation of the base members to be plated with periodic reverse current should be such as to produce a chemically clean surface as is conventional in order to secure the desired adherence of the metal to the base member. The preparation of the base member, therefore, may include brushing, grinding, sandblasting, shot blasting, degreasing, electrolytic cleaning and the like. Various types of base members may be plated. Metallic bodies on which metal may be plated from conventional electrolytes may be electroplated by periodic reverse current. Carbon and graphite forms may be electroplated. Electrotypes and electroforming base members consisting of wax or resinous patterns plated or coated with powdered graphite or precipitated silver may be electroplated as disclosed herein and the electrodeposited metal stripped therefrom. It will be found that electrotypes, molds and other electroformed members produced in accordance with the present invention will give a superior reproduction of the surface.

The electrodeposits produced by the use of periodic reverse current in accordance with the present invention may be plated subsequently with one or more other metals applied with similar periodic reverse current or by any other desirable process such as by continuous direct current. It is not necessary to use the same reverse current cycle in plating, but plating may be initiated with one cycle, then another employed, or the cycle may be changed a number of times to secure same desired effect. In many cases it has been found that the outstanding smoothness of the electrodeposits of the present invention enables the plating of subsequent metals even by continuous direct current or other conventional process to great advantage since the smoothness of the surface beneficially affects the subsequent plating which is equally smooth. Thus, we have been able to plate one layer of metal in accordance with periodic reverse current and thereafter plated nickel and chromium by direct current, and the nickel and chromium were so bright that no buffing was required. The periodic reverse current deposits produce metal deposits that are so homogeneous and free from pores and other flaws that they possess an improved corrosion resistance for a given thickness over the same metal applied by continuous direct current.

It is intended that all the matter contained in the above description shall be deemed to be illustrative and not limited.

I claim as my invention:

1. In the method of electroplating a metal from

the group consisting of iron, lead, indium, platinum, osmium, rhodium, iridium, palladium, ruthenium and alloys in which these metals predominate, on a base member from an aqueous electrolyte having the metal to be plated dissolved therein, the steps comprising applying a plating electric current to the base member for a period of time of not more than 40 seconds to electroplate an increment of the metal thereon, then applying a deplating electric current to the base member for a shorter period of time to deplate a substantial portion of the previously plated increment, the deplating electric current being of a magnitude and applied for a period of time sufficient to deliver from $\frac{1}{20}$ to $\frac{1}{2}$ of the coulombs delivered during the preceding plating period, and continuing the alternate plating and deplating until a desired thickness of the metal is applied to the base member.

2. In the method of electroplating a metal from the group consisting of iron, lead, indium, platinum, osmium, rhodium, iridium, palladium, ruthenium and alloys in which these metals predominate, on a base member from an aqueous electrolyte having the metal to be plated dissolved therein, the steps comprising applying a plating electric current at a given current density to the base member for a period of time of not more than 40 seconds to electroplate an increment of the metal thereon, then applying a deplating electric current of greater current density than the given plating current density to the base member to deplate a substantial portion of the previously plated increment, the deplating electric current being of a magnitude and applied for a period of time sufficient to deliver from $\frac{1}{20}$ to $\frac{1}{2}$ of the coulombs delivered during the preceding plating period, and continuing the alternate plating and deplating until a desired thickness of the metal is applied to the base member.

3. In the method of electroplating a metal from the group consisting of iron, lead, indium, platinum, osmium, rhodium, iridium, palladium, ruthenium and alloys in which these metals predominate, on a base member from an aqueous electrolyte having the metal to be plated dissolved therein, the steps comprising applying a plating

electric current to the base member for a period of time of not more than 40 seconds to electroplate an increment of the metal thereon, then reversing the direction of the flow of electric current for a shorter period of time to deplate a substantial portion of the previously plated increment, the deplating electric current being applied for a period of time sufficient to deliver from $\frac{1}{20}$ to $\frac{1}{2}$ of the coulombs delivered during the preceding plating period, and continuing the alternate plating and deplating until a desired thickness of the metal is applied to the base member.

4. In the method of electroplating a metal from the group consisting of iron, lead, indium, platinum, osmium, rhodium, iridium, palladium, ruthenium and alloys in which these metals predominate, on a base member from an aqueous electrolyte having the metal to be plated dissolved therein, the steps comprising applying a plating electric current to the base member for a period of time of not more than 40 seconds to electroplate an increment of the metal thereon, then applying a deplating electric current to the base member for a shorter period of time to deplate a substantial portion of the previously plated increment, the deplating electric current being of a magnitude and applied for a period of time sufficient to deliver from 15% to 40% of the coulombs delivered during the preceding plating period, and continuing the alternate plating and deplating until a desired thickness of the metal is applied to the base member.

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