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Link to Claims Section

May 8, 1956

Electroplating method

INVENTOR: RINES ROBERT H

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SUMMARY:

ELECTROPLATING METHOD

Filed Nov. 13, 1951 Inventor Robert H. Rines by J&t aa+JitAjt Attorneys Sheets-Sheet 1 May 8, 1956 R. H. RINES

ELECTROPLATING METHOD

Filed Nov. 13, 1951 l_l-/f PULSE

OSCILLATOR

Inventor Robert H. Rines Attorneys Sheets-Sheet 2 United States Patent Office Patented May 8, 1956 An additional object of the invention resides in the prevention of the formation of the before-described rippled plating effects caused

255973 (03) 2744860 May 8, 1956

by nodes and loops of the ELECTROPLATING METHOD

Robert H. Rines, Belmont, Mass.

Application November 13, 1951, Serial No. 255,973 i 11 tf\ tKd s\

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in an electroplating solution contained in a tank, shown in longitudinal section, and is vibrated magnetostrictively; Fig. 2 is a modification according to which the frequency The present mvention relates to electroplating. This application is a continuation-in-part of my co-pending application, Serial No. 608,780, filed August 3, 1945, now abandoned.

According to present-day methods of electroplating, continuous plating is hindered by the fact that, no sooner does the plating begin, then polarization effects commence to take hold and impede the plating process. A layer of positive hydrogen ions becomes deposited upon the surface to be plated, thereby interfering with the passing of the plating current. To overcome this difficulty, it has been proposed to agitate the solution betvveen the electrodes in the bath during the plating, thereby to break up the hydrogen-ion sheath. Other proposals have also been made, but the problem is still largely unsolved.

An object of the present invention is to provide a new and improved method of electroplating, which will not be subject to the above-described difficulties.

A further feature of the invention resides in a particular use of sonic or ultrasonic vibrations in the plating solution.

The dispersion effects of ultrasonics during the electrolysis of metallic particles has previously been observed.

An anode comprising the metal to be dispersed is usually within a vessel having cathodic walls containing 0 pages 190, 191.

the electrolyte. The cathode is ultrasonically vibrated, as by piezo-electric crystals, to cause the metal coming from the anode to become deposited in a somewhat finely divided form on the base of the vessel, or, alternatively, to be dispersed as an emulsion of the electrolyte. Ultrasonics have also been applied to electroplating systems, as distinguished from electrolysis-dispersion systems. Ultrasonic generators have, for example, been proposed for use as stirrers to agitate the electroplating bath and thereby to assist in maintaining uniform bath concentrations. It has also been observed that intense ultrasonic vibrations propagated vertically hi the region of the bath between the anode and cathode produce an increase in potential between the anode and cathode, just as though the solution pressure of the bath were increased. Ultrasonics have even been employed, propagated vertically between the anode and cathode in an electroplating bath, to produce standing vibrational waves that ripple the plating of the cathode, corresponding to nodes and loops of the vibrational waves, and afford measurement of the wavelength of the vibrational waves.

In accordance with the present invention, sonic or ultrasonic vibrations, hereinafter described by the term "sonic" which is thus intended to connote all such types of vibrations, are utilized in such a manner as not only to minimize the deleterious effects of ion sheaths but also, if desired, to provide for directional or selective control of plating at predetermined regions only of the cathode with the aid of appropriate directive vibrational fields.

Still another object of the invention resides in providing such directional selective plating effects without the necessity for masking or other similar techniques.

Mi7?4;+/vibrational waves propagated into plating media.

Other and further objects will be explained hereinafter and will be particularly pointed out in the appended will now be more fully described m connection with the accompanying drawings, Fig. 1 of which is a diagram of circuits and

apparatus embodying the mvention, in which the article to be plated is inserted of vibration is periodically varied; Fig. 3 is a horizontal section showing a further modification according to which a plurality of magnetostrictive vibrators are employed to produce selective plating results at predetermined regions only of a cathode being electroplated, and in which the oscillator driving the magnetostrictive vibrators is pulsed; and Fig. 4 is a similar view of an electroplating system employing a piezoelectric oscillator.

Referring to Fig. 1, a cathode article-to-be-plated 7 is shown partially immersed in an electroplating medium such as a solution 3 contained in a tank 1. An anode is also disposed in the plating solution 3 and is connected to the positive terminal of an electroplating source of potential 9, the negative terminal of which is connected to the cathode 7. The cathode 7 may, for example, be a flat disc of rectangular, circular or any other configuration. Secured to the center of the cathode 7 is a magnetostrictive rod or tube 4, centrally supported upon a conventional nodal support 21. A magnetostrictive oscillator 12 is connected with the magnetostrictive rod or tube 4 through the medium of two yokes or coils 13 an& lt;i 15 wound thereabout. The oscillator 12, the coils 13 and 15, and the rod 4 may have the form, for example, described by Pierce and Noyes in the Journal of the Acoustical Society of America, vol. 9, 1938, The cathode 7 may be set into a mode of transverse resonant vibration in accordance with which standing vibrational waves are propagated transversely along the cathode by driving the magnetostrictive vibrator rod or tube 4 secured thereto from the oscillator 12, the vibrations being thus directly applied to the article 7 without previous passage through the solution 3. The systern will oscillate at one of its modes of resonant vibration, the frequency of which is determined by the geometry and material of the cathode 7. The magnetostrictive vibrator tube or rod 4 preferably has a cross-sectional area small compared with the wavelength of the transverse vibrations in the cathode 7 in order that vibrations in the region of attachment to the cathode may be nearly in phase.

When such vibrating cathodes are inserted in an electroplating solution or bath they produce molecular vibrations between the vibrating portions of the cathode 7 and the corresponding adjacent portions of the solution 3. Maximum vibrations in the solution have been found to be produced not in the direction normal to the plane of the cathode 7, but in a direction at the Pierce angle with respect to the normal given by the equation sin 0=

where Vo is the velocity of propagation of the vibrational waves in the solution and V is the velocity of propagation of the vibrational waves in the cathode. For an aluminum cathode one-half inch thick, for example, vibrated in an aqueous plating solution at a frequency of thirty kilocycles, 6 is approximately 52 degrees.

As disclosed in the said copending application, if a cathode is vibrated molecularly during its electroplating, the effect of hydrogen ions sheaths will be found to be minimized and heavy plates will be produced in a more rapid interval of time than is possible without vibration.

A comparison of the quantity of plating produced per unit of time upon a stationary cathode and a similar molecularly vibrating cathode operating as shown in Fig.

1, showed a marked increase in the quantity of plating produced upon the latter over that produced upon the former. Such differential effects between vibrational and stationary plating have been found to exibt, indeed, for plating periods as short as twenty seconds that give rise to thin plates. These differential effects, moreover, have been produced by both audio and ultrasonic vibrational frequencies, though ultrasonic frequencies were found invariably to produce clean, substantial deposits. In no case, furthermore, was it observed that the plating was thrown off the cathode during its vibration or that there was evidence of metallic dispersion.

As an exainple, two highly polished aluminum strips, each an eighth of an inch thick, were partially inserted, side by side, into a saturated copper sulphate plating solution to serve as cathodes. The solution was formed in the conventional manner by dissolving about four ounces of crystalline copper sulphate in about one and one half quarts of water heated nearly to boiling, with a few drops of concentrated sulphuric acid added. Since the cathodes had to be formed with dimensions appropriate for convenient mechanical resonance for the existing oscillating equipment, it was desired that they be adaptable for repeated use. The metal aluminum was accordingly employed since copper plating

produced thereon may be relatively easily removed for purposes of further tests, as with the aid of steel wool or emery cloth. A copper anode 5 was placed about a foot from the cathodes, and a six-volt battery 9 was connected between the anode and the cathodes. One of the cathodes was connected at its center to a magnetostrictive tube 4, as shown in Fig.

1. The tube was driven by the before-mentioned Pierce magnetostrictive oscilaltor 12, setting this cathode mechanical resonance at an ultrasonic frequency of about kilocycles. After about two minutes of plating, the quantity and character of plating produced upon the vibrated cathode 7 was much superior to that produced upon the unvibrated cathode. The relative heaviness, fineness, clarity and uniformity of the plating of the vibrated cathode 7 were clearly discernible. The plate produced on the vibrated cathode, furthermore, appeared quite homogeneous and free of porosity. In addition, the plate was strongly adherent to the cathode In one sample, for example, it was found just as difficult to remove the plate a year and a half after it was formed as at the time of the vibrational electroplating. Such differential Dialing effects were also produced at an audio vibrational frequency of about kilocycles.

As a second example, a conventional chromium plat- 5o ing solution containing about grams of chromic acid per liter, and a few drops of sulphuric acid was employed. With the bath at a temperature of about C vibration, as shown in Fig. 1, by a magnetostrictive tube at a frequency of about kilocycles produced similar heavier deposits than without vibration.

As still a third example, similar vibration of a cathode at about 20 kilocycles in a 50 solution containing about 250 grams per liter of zinc sulphate with small dium acetate "5 will be set up in the solution between the cathode added, produced similar heavier zinc plates than without vibration.

Such a plating technique, however, may not be entirely practical for all commercial plating purposes since the nodal regions of vibrating cathodes may show up during longer periods of plating. Various techniques have been devised for eliminating these effects.

In Fig. 1, for example, a stirrer 2 is caused macroscopically to agitate the plating solution 3 while the cathode 7 is being molecularly vibrated, thereby to modulate the solution vibrations in accordance with the agitation pulsations to prevent the formation of standing waves in the solution 3 and thus to eliminate nodes and loops or ripples in the plating produced upon the cathode 7.

Stirring at the rate of a few revolutions per minute, as by a motor 6, has been found to eliminate nodes and loops in the above-described tests. The stirrer 2 may be inserted into the bath 3 through the bottom wall of the tank 1 within a liquid-tight seal 8, as of rubber, that may serve as a bearing surface for the shaft of the stirrer 2.

Other well-known stirring arrangements may also be utilized. Unless this agitation takes place in close vicinity to the cathode 7, however, the standing vibrational waves set up in the solution 3 by the molecular vibration of the cathode 7 in response to the action of the magnetostrictive oscillator 412 will still produce the standing-wave pattern that gives rise to the before-mentioned undesirable ripples in the plating. To prevent this it has been found very effective to cause the stirring motion to be effected within a few inches of the cathode 7.

Another technique that has been evolved for preventing the node-and-loop or ripple formation on the cathode 7 being electroplated is illustrated in Fig. 2. In this case, the complete cathode 7 is immersed in the solution 3 and the magnetostrictive rod 4 is provided with a water-tight housing, 14, such as the conventional underwater signalijng housings, surrounding at least a portion of the rod and containing the energizing coils 13 and 15. It is to be understood, of course, that the complete cathode 7 and driving rod 4 may similarly be immersed in the plating solution in the embodiment of Fig. 1. The coil 13 is connected in the plate circuit of a vacuum tube 17 in the manner of the conventional Fierce-type magnetostrictive oscillator 12, before mentioned, and a condenser 10 is connected in parallel with the coil 13. The coil 15 is connected in the grid or input circuit of the oscillator tube 17_ This oscillator 12 is provided with means for periodicauy varying its frequency within specified limits, thereinto 40 by producing successive frequency-varying pulses. In tlljs case& gt; rotor of tjbie condenser is periodically rotated by a motor 16 to tune the

oscillator system over a band of frequencies and thereby to cause the frequency of transverse vibration set up in the cathode 7 to vary accordingly. As an illustration, the frequency of a system 4__12 operating in the neighborhood of twenty kilocydes has been periO(3iCally varied at a rate of a few times a secOnd within limits of plus or minus two hundred cycies Tk;s tuning process has been found also to prevent fte formation o standing waves in the solution 3 and, h ft itg the molecular vibrations to dispel the formation of the rip-

Ple f n des and loP! th5 P!atm.g Fuced upon the K_ cattlode 7 over lonS Penods of operation.

As ls also described in the said copending application, the deslred molecular vibrations may be produced in other wayg m bV securing the vibrator directly to the cathode 7- % placing the vibrator 4 at a point spaced from one face of a thin cathode 7, as illustrated in Fig. 3, for exam-

Pie, vibrations may be produced of frequency determined by the dimensions of the magnetostrictive rod or tube 4 and not by the dimensions of the cathode 7. If the rod or tube 4 is maintained with its axis substantially normal to the plane of the cathode 7, standing vibrational waves the magnetostrictive rod or tube 4 in the region of the solution external to the region between the cathode 7 and the anode 5. Since the vibrational waves produced by the rod or tube 4 are fairly directive, resulting from lengthwise magnetostrictive expansions and contractions of the rod or tube, the selected predetermined region of the cathode disposed opposite to the end of the magnetostrictive rod or tube will be subjected to intense vibrational waves while other regions of the cathode are not so affected.

This has been found to result in selective plating in the predetermined region of the cathode 7.

If desired, furthermore, a plurality or array of vibrators 4, 4, may be utilized to produce intense vibrational disturbances at a plurality of predetermined points along the cathode 7. This type of operation, as described in the said copending application, has been found to result in the production of selective plating effects at the regions of the cathode 7 corresponding to those regions disposed opposite to the ends of the vibrators 4 and 4.

In one test, as an illustration, a plane rectangular brass cathode 7 about an inch and a quarter by an inch, and about a sixteenth of an inch thick, was polished only on one surface and completely immersed in the before-described copper sulphate plating solution 3 with the polished surface facing the anode 5. The magnetostrictively vibrated element 4, about a half inch in cross section, was placed in the solution adjacent the unpolished surface of the cathode so that it vibrated in the direction substantially perpendicular to the plane of the cathode 7. The vibrator element was spaced about an eighth of an inch from the unpolished cathode 7 at a point about a half an inch from one end of the cathode, somewhat as illustrated by the vibrator 4 in Fig. 3. After about ten minutes of plating in the above-described solution, a markedly heavier plating was observed on the polished surface of the vibrated end of the cathode than upon any other portion of the cathode. The region of increased plating, moreover, was clearly limited to about an inch square, in the immediate vicinity opposite the vibrated element.

Similar directional results have been observed with the before-described chromium and zinc plating solutions.

Such directional effects have also been produced with piezoelectric vibrators placed near predetermined regions of the cathode during electroplating, as illustrated at in Fig. 4.

These directional or heavier plating effects have thus been produced without the necessity for masking and other types of shielding devices. If, for example, it is desired to plate a particular portion of a utensil, such as silverware, with a heavier plate than the other regions of the utensil, by directing an appropriate directional vibrational field in the vicinity of the place where it is desired to produce the heavier plating, such heavier plating may automatically be produced to the effective exclusion of all other regions of the cathode.

The rippling effects caused by nodes and loops of the vibrational waves may be eliminated in such directional plating operations in the same manner as before discussed in connection with the embodiments of Figs.

Such rippling effects have also been found to become obviated by amplitude pulsing the oscillator 12. By interrupting the plate supply of the oscillator 12, or by periodically applying cut-off pulses to the oscillator grid circuit by a square-wave generator 21, as is well-known in the radar and other pulsing arts, the oscillator 12 can be caused to operate periodically, thereby to produce in a preferred and highly controllable manner the desired vibrational disturbances periodically without the formation of standing waves in the solution 3. In the above-described experiments, for example, pulsing the oscillator at a frequency of about ten times per second has been found effectively to eliminate the rippled plating effects caused by nodes and loops set up by standing vibrational waves. This same pulsing technique may, of course, be substituted in the systems of Figs. 1 and 2 for the stirring and tuning techniques therein respectively disclosed.

It has been found that more uniform plating is obtained and better control is effected over the shaipness of the directional plating when the vibrational apparatus is positioned in the region external to the portion of the electroplating solution between the anode and the cathode, as illustrated. This is apparently true because alterations in the plating potential gradients, in vibrational field patterns and in the concentration and other properties of the plating solution between the anode and cathode are thereby effectively prevented.

In all the above-mentioned tests, moreover, the magnetostrictive or piezoelectric vibrators are described and illustrated as oriented in the direction substantially normal to the plane of the cathode or substantially parallel to the electric field between the anode and cathode. This direction has, in practice, been found preferable for produring the most sharply defined directional plating effects.

The explanation for this may reside in the following considerations:

First, for the production of directional effects, it appears that the fairly directive beam of vibrational waves should be impinged normal to the article and hence parallel to the electric field in order to confine the intense disturbances to as small a region of the article as possible.

Secondly, since the deleterious ion sheaths are believed to be formed during plating by the migration of the metal ions toward the cathode along the lines of electric field intensity, it would appear most effective to produce periodic disturbances along the direction of current flow to prevent the formation of the ion sheaths.

In the case of the vibrator secured to the cathode, best impedance transformation of the vibrational energy can be effected by the orientation of the vibrator normal to the plane of the cathode.

A significant clue to the probable explanation of the above-described results resides in the observation of the constant agitation of the bubbles near the cathode 7 when such vibrations are employed. It appears likely that ion sheaths, that quickly plague cathodes being electroplated in the conventional manner, are continuously prevented from forming during vibrational plating, so that the plating continues unimpeded apparently indefinitely.

This may explain the faster plating observed during vibration.

As for the directional effects, since directional vibrational fields can prevent the formation of ion sheaths only where they exist, only the region of the cathode subjected to these fields, or at least to the intense portions of the fields, will be selectively plated in this manner. Obviating the rippled effects caused by the setting up of nodes and loops, by the various techniques above-described, furthermore, permits the application of these teachings to long periods of plating, as well as to short plating periods.

As explained in the said copending application, if it is desired that vibrational disturbances be produced over the complete cathode area, this may be done by disposing and 2. 50 a plurality of vibrators spaced from the cathode at various closely positioned predetermined positions somewhat in the manner illustrated in Fig. 3, though with a great many more vibrators. This effect may also be produced by disposing a vibrating plate substantially parallel to the cathode, or, for maximum effects, at the before-mentioned Pierce angle thereto. The effect may also be produced by

vibrating a wall of the plating tank disposed substantially parallel to the cathode or, for maximum effects, at the Pierce angle thereto. In all cases the nodes and loops may be prevented in various degrees by the macroscopic simultaneous stirring technique in the region of the cathode 7, as illustrated in Fig. 1, the periodic tuning technique illustrated in Fig. 2, or the preferred amplitude pulsing technique illustrated in Figs. 3 and 4.

Further modifications will occur to those skilled in the art, and all such are considered to fall within the spirit and scope of the invention as defined in the appended claims.& lt;/

ENGLISH-CLAIMS:
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claims.

What is claimed is:

1. An electroplating method that comprises electroplating an article disposed in an electroplating solution, during the electroplating, producing sonic vibrations and applying the same to produce a relative vibration of molecular amplitude between a predetermined region of the article at which it is desired to produce a greater degree of vibration than at other regions of the article and a predetermined region of the solution at the surface between them, and confining the vibrations to periods of successive discreet pulses in order to prevent the formation of standing vibrational waves between the article and the solution.

2. An electroplating method that comprises electroplating an article disposed in a: i electroplating solution, during the electroplating, producing sonic vibrations end applying the same to produce corresponding vibrations between a predetermined region of the article and a predetermined region of the solution at the surface between them, and confining the vibrations to periods of successive discreet pulses in order to prevent the formation of standing vibrational waves between the article and the solution.

3. An electroplating method that comprises electroplating an article disposed in an electroplating solution, producing a directional beam of sonic vibrations, during the electroplating directing the directional beam of sonic vibrations upon a predetermined region only of the article m the solution to produce a selective molecular vibration between the predetermined region of the article and the corresponding region of the solution, thereby selectively to control the plating at the said predetermined region of the article, and confining the vibrations to periods of successive discreet pulses in order to prevent the formation of standing vibrational waves betv/een the article and the solution.

4. An electroplating method that comprises electroplating an article disposed in an electroplating solution, during the electroplating producing sonic vibrations and directing the same to produce corresponding vibrations between a predetermined region of the article and a predetermined region of the solution at the surface between them, and confining the vibrations to periods of suecessive discreet pulses.

5. An electiopiating method as claimed in claim 4 and in which the said vibrations are applied at an angle 8 to the direction normal to a plane of the article given substantially by the equation sin 0=

ciety, July 1945, pp. 688-90.

wheie Vo is the velocity of propagation of the vibrations in the solution, and V, the velocity in the article.

6. An electroplating method as claimed in claim 4 and in which the said vibrations are applied directly to the article without previous passage through the solution.

7. An electroplating method as claimed in claim 4 and in which the said vibrations are produced at a frequency corresponding substantially to a mechanical resonant frequency of the article.

8. An electroplating method as claimed in claim 4 and in which the said vibrations are produced in a directive beam.

9. An electroplating method as claimed in claim 4 and in which the said vibrations are produced in a plurality of directive beams.

10. An electroplating method as claimed in claim 4 and in which an anode is disposed in the electroplating solution between which and the article an electroplating current flow is established, and the said vibrations are produced in a direction having a component substantially parallel to the said current flow.

11. An electroplating method as claimed in claim 4 and in which the said pulses are frequency-varying pulses.

12. An electroplating method as claimed in claim 4 and in which an anode is disposed in the electroplating solution between which and the article and electroplating current flow is established, and the said vibrations are produced in a region external to the region of the solution between the anode and the article.

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