United States Patent

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Continuation-in-part of application Ser. No. 718,468, Apr. 3, 1968, now abandoned.

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[54] **APPARATUS FOR ELECTRODEPOSITION**
9 Claims, 7 Drawing Figs.

[52] **U.S. Cl.** **204/217,** 204/227, 204/DIG. 10
[51] **Int. Cl.** **B23p 1/00**
[50] **Field of Search** 204/14, 29, 35, 36, 106, 200, 203, 215, 225, 226, 280, 287, 207, 208, 227, 224

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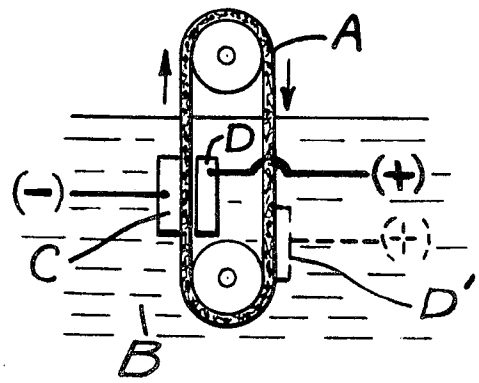
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Assistant Examiner—R. J. Fay
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ABSTRACT: Electrodeposition apparatus where, in addition to the conventional cathode, anode and electrolyte supply means, there is also provided a nonconductive hard particle activating means and associated driving means to contact the surface of the electrodeposit under controlled pressure throughout its formation and to both activate the surface of the electrodeposit and also to maximize the supply of fresh electrolyte directly to the activated surface.



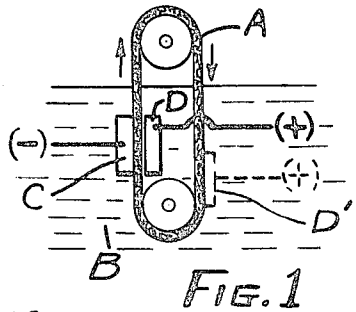


FIG. 1

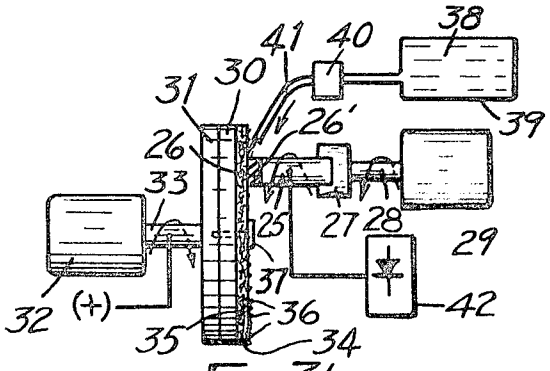


FIG. 3'

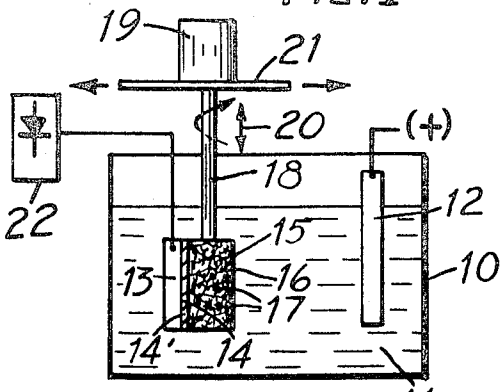


FIG. 2

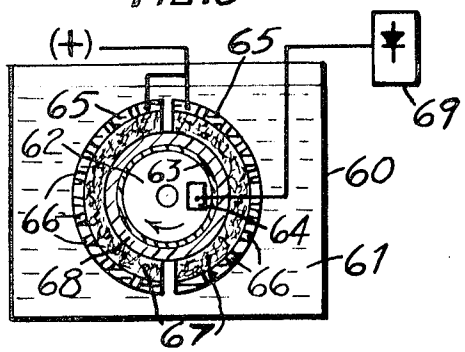


FIG. 5

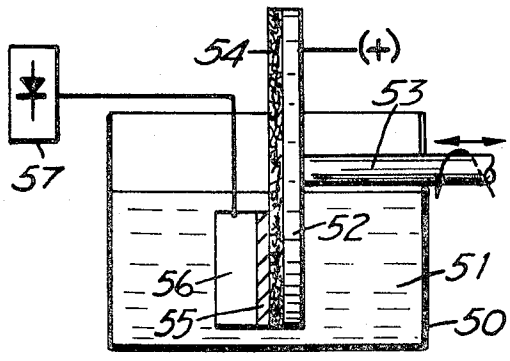


FIG. 4

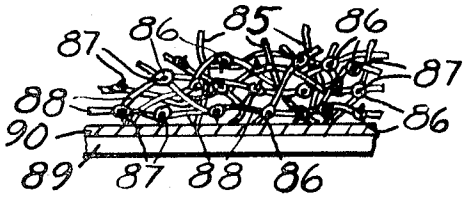


FIG. 7

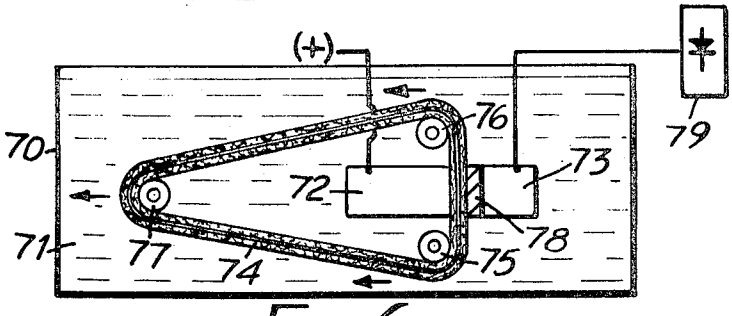


FIG. 6

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APPARATUS FOR ELECTRODEPOSITION

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of my prior, copending application, Ser. No. 718,468, filed Apr. 3, 1968 and entitled Electrodeposition (now abandoned).

FIELD OF THE INVENTION

Electrodeposition of metal on another surface through electrochemical action, has been generally a slow process. Particularly, this has been true in the production of dense, smooth, compact platings from aqueous solutions containing dissolved salts of the metal to be deposited. The present invention relates to this general field of electrodeposition and includes the specific fields of electroplating, electrowinning, electrorefining and electroforming.

DESCRIPTION OF PRIOR ART

Many efforts have been made in the past to speed up such electrodeposition processes but these have, in the main, met with only limited success. The chief reason for this is the existence of a limiting current density for all aqueous metal plating baths, such limit being determined by the concentration, temperature, transport number of the metal ions, the thickness of the polarization layer at the cathode or surface being plated, and particularly by the local increase in current density at asperities formed on the surface deposit. Efforts to increase the limiting current density (and resultantly the speed of deposition) have generally revolved around changes in the type of anion, increase in the amount of metal ion concentration in the electrolyte, the use of higher electrolyte temperatures, and solution agitation, including greatly increasing the flow rate of the electrolyte solution. These efforts have not solved the problem of increasing speed of deposition to any appreciable extent.

Generally the art has failed to recognize the concept on which the present invention is built. Hard particle contacts have been made with surfaces to be electroplated but generally only prior to actual electroplating for purposes of cleaning the surfaces or for other reasons and once the deposit commences to form the hard particle contact is discontinued. Apparatus of this type does not contain the means for controlling the pressure of the activating means and does not provide for continuous activation during formation of the electrodeposit. Further, apparatus has heretofore been provided to continuously or intermittently move a surface over an electrodeposit. Such surfaces have, however, generally been of the nonparticle containing type typified by example 7 hereof. Hence, these types of apparatus have been lacking in the requisite hard particle supporting means critical to the success of the present invention.

SUMMARY

The present invention is directed towards apparatus for use in a process in which the current density is high compared with that of conventional processed, e.g., 20,000 amps per square foot vs. 10 amps per square foot for conventional tin plating, and in which the apparatus causes the surface or the deposit to be repetitively contacted at extremely short time intervals by what is termed herein as "dynamically hard" particles. By this term is meant that the combination of the hardness of the particles, the contact pressure of the particles on the surface of the electrodeposit and the speed at which such particles are moving relative to the electrodeposit surface is such as to produce an action on such surface sufficient to mechanically "activating" the surface. "Activating" the surface of the electrodeposit within the meaning of the present invention requires the generation of new surface defect sites through mechanically distorting the crystal lattice of the metal deposited. It is believed that the mechanism is rather complex and and consists of several actions taking place essentially simultaneously. First, there is the new surface defect site generation resulting from distortion of the crystal lattice structure as mentioned above. This provides growth sites for many more asperities than would be the case absent this mechanical distortion. Additionally, any dominant asperities already formed are cut off or bent over and crushed by the dynamically hard particle contact. These two actions result in substantial elimination of the current robbing which takes place at the asperities formed in normal plating and is believed to be one of the major contributing factors to the ability to maintain high current densities for substantial periods of time while maintaining acceptable deposits with this process. Further, the action of the activating medium is believed to result in the removal or substantial diminution of the stagnant polarization layer overlying the electrodeposit surface and to maintain a high concentration of metal ions adjacent such surface due to the pumping action of the activating medium which carries a supply of fresh electrolyte across the electrodeposit surface at a high flow rate.

The apparatus requires as an essential element thereof a surface disturbing or activating means providing a plurality of small, dynamically hard, relatively inflexible particles held in substantially fixed, spaced relationship to one another and generally vertical to the surface receiving the deposit by a preferably porous matrix or supporting member which also provides a plurality of surfaces extending parallel with and closely adjacent to the surface being plated. The apparatus further provides relative motion during the deposition operation between the surface receiving the deposit and the activating means and, if desired, between one or more of the electrodes and the activating means. In addition, sufficient pressure is applied by the apparatus to said activating means in a direction normal to the electrodeposit surface to cause mechanical distortion of the crystal lattice structure of the metal deposited thereon. The spacing of the particles and the speed of relative movement provided by the apparatus is such that the deposited metal surface above any given point on the cathode surface is contacted or influenced by a particle at extremely short time intervals, e.g., intervals in the range of 6.1×10^{12} to 3.8×10^{17} seconds. Fresh electrolyte is supplied to the zones of activated metal deposit at the same rate through entrapment by those surfaces of the activating means (which surfaces may be the edges of the particles) parallel with the electrodeposit surface. These surfaces, when the apparatus is in operation, sweep fresh electrolyte along with them, the electrolyte reaching such surfaces due to the porosity of the supporting matrix of the activation means or through the proper disposition of the electrolyte feeding means.

Accordingly, the principal object of the present invention is the provision of high speed electrodeposition apparatus for the deposition of metals on a conductive substrate. The term "electrodeposition" is intended to cover not only submersion within a bath but also the provision of a continuous flood of electrolyte over the deposit surface during deposition external of the physical confines of the usual tank used as a bath.

DRAWINGS

FIG. 1 illustrates schematically the general type of apparatus of the present invention.

FIG. 2 is a schematic illustration of another embodiment of the apparatus of the present invention applied to bath electroplating.

FIG. 3 shows schematically the arrangement for flooding the electrodeposit surface with electrolyte apart from any bath as such and a variation of the present apparatus as applied to such an arrangement.

FIG. 4 illustrates schematically an application of the present apparatus in the electrowinning of copper.

FIG. 5 illustrative of the present apparatus applied to the electroforming of a nickel cylinder.

FIG. 6 is a schematic representation of the present apparatus utilized in the electrorefining of copper.

FIG. 7 illustrated diagrammatically a portion of a cross section of one type of porous activating means useful in the present invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

The apparatus of the present invention requires, in combination, means for the controlled application under pressure, both normal to and parallel with an electrodeposit surface continuously during its formation, of a supporting, preferably porous, matrix which supports in closely spaced relationship a plurality of small, relatively inflexible particles; means for generating an electric current; electrode means between which said current is caused to pass; means to supply electrolyte between said electrodes; and means to cause continuous relative motion between said activating medium and the surface of said electrodeposit and/or the surfaces of one or more of said electrodes during the passage of said current and the formation of the electrodeposit. The particles are so positioned in the matrix as to contact the deposit forming on the cathode surface and, in some instances, to contact the anode surface. The cathode surface, itself, is normally covered during electroplating with a relatively stagnant layer of electrolyte which may be identified as the diffusion or polarization layer. The thickness of this layer, even at high flow rates of electrolyte or turbulent agitation of a plating bath, is at least 0.001 centimeter. Under application of the support matrix and associated particles according to the present invention, this polarization layer is repetitively removed or its thickness substantially diminished repetitively through the plating cycle. As described above, the apparatus activates the electrodeposit surface by multiplying many times the number of nucleation sites on such surface and generating a controlled growth of a tremendous number of very short asperities which are repetitively restricted in vertical growth throughout the deposition cycle. The metal deposit reflects this action since photomicrographs of the cross sections of such deposits illustrate a structure in which the growth axis of the crystals appears substantially parallel to the substrate rather than showing the normal columnar vertical orientation of conventional electrodeposits.

Using this apparatus it has been found possible to increase the limiting current density many times beyond that possible with electrodeposition apparatus heretofore available, resulting in much more rapid metal deposition than is possible with such other equipment. The present apparatus has further been found to produce a hard, dense, smooth metal deposit. These results are achieved even though practical application of the apparatus may result in minor metal removal from the deposit on the cathode surface, cutting down slightly the total thickness of such deposit This metal removal is minimized by control of the pressure to produce a light scratch pattern in the metal deposit. Thus the dynamic hardness of the particles may be substantially grater than the actual hardness, e.g., a resin particle may produce a scratch in a much harder nickel deposit. This scratch pattern may be visible to the naked eye but, in any case, will be seen under a magnification of 10,000 power or less. While the scratches may be produced by metal removal, preferably the dynamic hardness is so controlled that a displacement of metal atoms on the surface rather than actual removal is the basis for the scratch formation.

By using small, relatively inflexible, non conductive particles as the activating tool, no spot on the deposit surface is covered for any appreciable length of time by the activating particle. Further, since the activating particles are fixed to the supporting matrix, there is no danger of a particle being occluded as a crack-initiating impurity in the electrodeposit. These particles are generally randomly distributed over at least the cathode surface contacting side of the matrix and are preferably spaced in fixed relation to one another over very short spans, e.g., 1.25×10^{11} inches to 5.65×10^{14} inches. If desired, accurate and non random distribution of the particles on the supporting matrix can be resorted to although this is generally an unnecessary complication. By the term "particle" as is used herein is meant not only completely separate and discrete three dimensional bodies, but also larger bodies with a plurality of points, tips, projections or the like thereon as for instance a relatively hard resinous coating on a fiber wherein the coating contains multiple irregular spaced projections and is generally uneven in nature. The particles, as described herein, contact or at least influence essentially all of the surface of the electrodeposit throughout its formation and are believed to knock down or cut off as they form most of the dominant asperities on such surface. The particles themselves may vary widely in size from 1×10^{15} inches to 1.25×10^{11} inches (average diameter) for example, but should generally be in the size range of from 9×10^{14} inches to 2×10^{12} inches for best results. The particles can generally be defined as hard, i.e., having a Knoop hardness in excess of 10.0, but the degree of hardness per se is not critical except that control should be exercised not to use a product which is too abrasive for the particular metal being deposited. The degree of pressure applied must also be considered with respect to the hardness of the particles and generally with the softer range of particles more pressure normal to the cathode surface is required than with the harder range of particles.

As indicated above, the controlling factor is the dynamic hardness of the particles i.e., the apparent hardness resulting from a combination of the actual Knoop hardness, the pressure applied and the speed with which the particles are moved across the electrodeposit. A visible indication that the dynamic hardness is sufficiently high is the presence in the deposit of the scratches visible under 10,000 x magnification.

The most graphic effect of the present apparatus is the increase in practical limiting current density achieved. As is well known, the current density is directly related to the speed of metal deposit. The limiting current density is achieved when the application of increased voltage ceases to result in any substantial increase in current flow. This current flow will increase again sharply at higher voltage but this is due to other reactions at the cathode, e.g., dissociation of water, etc. While interesting, this limiting current density is not necessarily a practical measure of plating rate since useful metal deposit in conventional electrodeposition processes will stop at a level below the limiting current density (practical current density). By use of the present apparatus, not only does the limiting current density appear to be also the practical current density, but such current density is substantially above the limiting current density for conventional processes.

The matrix used to support the activating particles is preferably electrolyte-permeable, having a through porosity in the order of at least 6.5 Sheffield units (as measured by a Sheffield porosimeter using a 2¼-inch ring). Preferably, this matrix is also at least somewhat compressible and deformable so that it can be conformed to irregular surfaced cathodes and associated deposits where necessary. As indicated above, the matrix is required to have a plurality of thin walled surfaces extending between the activating particles to act as electrolyte sweeps. While these surfaces may be the edges of the particles themselves, in the preferred embodiments, these thin-walled surfaces, formed by the porous matrix, define small compartments or pores of either regular or irregular shape which function much like a bucket conveyor in carrying small quantities of electrolyte over the activated electrodeposit surface. Many variations of porous supporting matrices have been used, e.g., open mesh screens with activating particles adhered to the mesh; nonwoven abrasive articles, both compressed and uncompressed; open cell foam sheets with the activating particles incorporated in or on the foam cell walls; sponge materials containing the required particles and the like. Examples of products which can be used in the present invention as activating media are illustrated in U.S. Re. 21,852 to Anderson which shows an open mesh product having abrasive grains adhered thereto; in U.S. Pat. No. 3,020,139 to Camp et al. which illustrates nonwoven webs having a plurality of hard particles adhered to and along the web fibers; in U.S. Pat. No. 3,256,075 to Kirk et al. which illustrates a sponge containing hard resin impregnated sponge particles; and in U.S. Pat No. 3,334,041 to Dyer et al. which illustrates a coated abrasive product having perforations through which electrolyte can flow. In this latter instance, the product must be modified for use with the present apparatus by making it nonconducting,

i.e., it essentially becomes a standard coated abrasive product with electrolyteipassing holes therethrough.

In some instances a nonporous matrix may be desirable. This is particularly true when it is desired to reduce the anode-cathode spacing to a minimum. A suitable nonporous product is illustrated in U.S. Pat. No. 3,377,264 to Duke et al. wherein a coated abrasive sheet is provided with a front conductive layer of metal through which protrude the tips of nonconductive abrasive grains. This product for use with the present apparatus must have as the conductive layer of metal an insert metal such as lead or antimony or alloys thereof. The tips of the abrasive particles cooperate with the metal layer therebetween to form compartments which serve as electrolyte sweeps to move the electrolyte to the face of the electrodeposit. With this product it is essential that the electrolyte be supplied to the face of the product immediately adjacent the point of contact with the electrodeposit similar to the illustration of FIG. 3 hereof. Similarly, the product of the aforementioned Dyer et al. U.S. Pat. No. 3,334,041, may be used with rivets or similar conductive paths provided from the back to the front surface and the current applied to the back of the product.

Referring now to FIG. 1 of the drawings, the minimal elements of the apparatus of the present invention are disclosed and identified by legends. As shown, a particle supporting means A (here shown in porous, endless belt form) is provided in combination with an electrolyte B and electrodes C and D. Relative motion between the porous means A and the cathode surface (or the plate depositing thereon) and, if desired, between such porous means A and the anode surface D (shown in dotted lines as D' for this variation) is provided as shown by the arrows. This relative motion continues throughout that portion of the plating cycle when high speed deposition is required.

Referring again to the drawings, FIG. 2 is a schematic plan view of one form of the apparatus of the present invention applied to a bath type electroplating system. The electrolyte 11 in container 10 may be any of the conventional plating solutions known to the art. Positioned in the electrolyte are electrode means 12 and 13 comprising an anode 12 and a cathode 13 connected to means 22 for supplying current thereto. The cathode 13 is the member to be plated and that portion thereof which it is desired to plate is suspended in the electrolyte bath 10. Adjacent to the face 14 of the cathode 13 to be plated is the activating member. As illustrated, this is a drum or cylinder 15 of porous material such as nonwoven fibers 16 having a plurality of small, hard particles 17 adhered to the fibers 16 by a suitable adhesive. Drum 15 is mounted for rotation on a shaft 18 drived by a suitable motor 19. If desired, the drum 15 may also be oscillated up and down as illustrated by the arrows 20 as well as rotated. Motor 19 and the associated shaft and drum assembly can be moved laterally on support 21 to vary the pressure applied to the cathode 13 by the activating drum 15. Rotation of the drum 15 initially against the face 14 of cathode 13 and thereafter against the electrodeposit 14' causes the previously described activation of the electrodeposit layer 14' which builds up on the face 14. This rotation, which continues for the time the electrodeposit 14' is forming, also causes fresh electrolyte to be pumped across the face 14' of the deposit by the entrapping action of the fibers forming the porous cylinder 15.

FIG. 3 illustrates a schematic form of the apparatus of the present invention showing the use of electrode flooding means for supplying the electrolyte. Here the workpiece to be plated 25 is a cylindrical shaft, the end 26 of which is to receive the plate. Shaft 25 is connected to the negative side of a power supply 42 to form a cathode and is mounted for rotation in a chuck 27 at the end of a shaft 28 of a motor 29. The anode in this instance is a plate, e.g., of lead 30 mounted on a suitable rotating conductive backup plate 31 which in turn is rotated by motor 32 through shaft 33. Positioned on the outer surface of anode plate 30 is a porous activating member 34 in the shape of a flat disc. This member 34, which is illustrated as a mesh screen 35 having hard particles 36 adhered to the mesh surfaces thereof, is held on anode plate 30 by a bolt 37 which is threaded into the backup plate 31 and serves also to hold the anode 30 on such backup plate 31. The anode is connected to the power supply through shaft 33 as illustrated. Electrolyte 38 is fed from a reservoir 39 by means of a pump 40 and associated tubing 41 into the interface between the anode 30 and the superposed electrodeposited surface 26' on cathode face 26. The electrolyte is also carried by the cells formed in the mesh activating member 34 as it rotates. The pressure of the cathode 25 on the mesh surface of the activating member 34 can be adjusted by relative movement towards or away from the rotating plate 31 to regulate the dynamic hardness as described above.

FIG. 4 schematically illustrates apparatus used in electrowinning copper from a leaching solution of copper and sulfuric acid. The apparatus is positioned in a tank 50 containing the leaching solution 51. A rotating inert lead anode disc 52 is mounted on drive shaft 53. Adhered to the face of the anode 52 is a porous media containing spaced particles as described herein. This activating medium 54 is in contact with the electrodeposit 55 of copper forming on the face of cathode 56 which is connected to power supply 57. As the electrodeposit grows, the shaft 53 may be moved away from the cathode 56, keeping a constant pressure between the activating medium 54 and the electrodeposit 55, if desired,

FIG. 5 illustrates the application of the present invention to the electroforming of a particular shape—in this instance a cylinder. The apparatus is positioned in a tank 60 containing a plating solution electrolyte 61. Rotatably positioned in the solution is a stainless steel forming mandrel 62. This mandrel carries a thin (usually flash-coated) deposit 63 of the metal to be formed in order to permit separation of the subsequently deposited metal from the mandrel 62. Mandrel 62 is made the cathode by contact with a brush 64 connected to the negative terminal of the power supply 69. Positioned in the solution and around mandrel 62 is a split ring, expandable, inert anode member 65 which contains a plurality of perforations 66 in the surface thereof to permit passage of the electrolyte. Adhered to the inside surface of the anode member 65 is a porous activating member 67 of the type described elsewhere herein. As shown, the activating medium 67 is in contact with the deposit 68 which is being built up around mandrel 62. As the deposit increases in thickness, split ring anode 65 expands permitting control of the pressure between the activating medium 67 and the electrodeposit 68. When the desired thickness is achieved, the anode is removed and the cylinder separated from the forming mandrel.

FIG. 6 illustrates the present invention as applied to the electrorefining of an impure metal. The apparatus is positioned in tank 70 containing electrolyte 71. An impure metal anode 72 is moveably mounted within the electrolyte in contact with a porous activating medium in the form of a continuous belt 74. Power supply 79 connects to cathode 73 of the metal to be deposited which is in contact with the other side of belt 74 initially, but at the point in the deposition cycle illustrated in FIG. 6, has the belt 74 interposed in contacting relationship between anode 72 and the deposited layer of pure metal 78 on cathode 73. Belt 74 rotates on idler rollers 75 and 76 and driver roll 77. The belt and associated rollers are capable of adjustment away from the surface of cathode 73 as the deposit 78 builds up. In operation, the activating belt wipes both the electrodeposit surface for the reasons hereinelsewhere described in detail and also the surface of the anode whereby the anode is assisted in more rapid dissolving.

FIG. 7 shows a highly enlarged and idealized portion of one type of activating media suitable for use in the present invention and illustrates the hard particle-connecting matrix relationship. Reference numeral 85 represents fibers of a nonwoven web (nonconducting fibers such as polyethylene terephthalate or the like) which are anchored one to the other at their points of intersection by an adhesive binder 86. A plurality of small, hard, discrete particles 87 are positioned on the

fibers 85 and in the present illustration are held to such fibers by the adhesive 86. At least some of the fibers 85 extend relatively parallel to the cathode face 89 as shown at 88 to form the thin-walled cells or electrolyte sweeping members referred to above. (For purposes of illustration, the activating particles 87 are here shown at some distance from the cathode face 89 and associated electrodeposit 90 although in operation of the present apparatus they would be in contact therewith.)

EXAMPLE 1

A porous activating device was made up by first forming on a Rando-Web machine (as described in U.S. Pat. No. 3,020,139 to Camp et al.) a nonwoven web from 40 denier Dacron fibers of 2 inch fiber length. The web was spray bonded with an acrylonitrile-melamine resin adhesive to bind the fibers to one another at their points of intersection. The prebonded web was then roll coated with a phenolic adhesive under a pressure of 40 p.s.i. The saturated web was then placed between plates and compressed from an initial thickness of three-fourth inch to one-sixteenth inch thickness while wet and dried for two hours at 250° F. The web was then subjected to a temperature of 315° F. for 15 minutes to cure the adhesive. Void volume on the finished web was measured at 85 percent with many openings through the web from one surface to the other. The roll coating had deposited the phenolic resin adhesive along the fibers in uneven fashion with many spaced projections and these hard resin projections or particles were found to have a Knoop hardness of 43. The particles were very irregular in size.

The activating material was then formed into a 7-inch circular pad approximately one-sixteenth inch thick and clamped against a 7-inch diameter lead disc anode. The anode was mounted on the end of the shaft of a variable speed motor and was rotated while a jet of electrolyte formed from a mixture of 49.5 oz./gal. of $NiSO_4 \cdot 6H_2O$ and 2 oz./gal. boric acid was forced onto the surface of the pad at a flow rate of 0.5 gal./minute. A ½-inch diameter type 1018 steel rod rotating in the opposite direction to the anode at a rate of 40 r.p.m. was then pressed against the activating pad at a pressure of 26 p.s.i. The rotating anode was contained inside a closed chamber having one port for the anode-driving shaft and a second port or opening for the introduction of the rod. The electrolyte jet was introduced into this chamber and a means for draining the electrolyte into its original container for recirculation was provided at the base of the chamber. The one-half inch diameter rod which serves as the cathode was connected to a 1,500 ampere, 48 volt selenium rectifier as power supply. The disc speed was 1,000 surface feet per minute while the plating temperature was held at 170° F. Using a current density of 2,160 amps per square foot, a 2 mil thick smooth, compact nickel deposit was achieved in 60 seconds. The surface of the deposit showed a mild scratch pattern to the naked eye.

EXAMPLE 2

Using the same equipment arrangement as in example 1 (which is illustrated in FIG. 3 of the drawings), the activating pad of example 1 was replaced with an open mesh abrasive product using a 21×20 mesh/in.^{2}, nylon fabric as the supporting porous media. Anchored to this by a phenolic adhesive was a coating of closely spaced grit 400 aluminum oxide particles. Since this was a commercial product designed for maximum stock removal, the mesh disc, before using in the present process, was deliberately dulled by running it against a 304 stainless steel surface for 7 minutes at 20 p.s.i. and 1,000 surface feet per minute. The abrasive material was similar to that described in Re. 21,852 to Anderson.

Using the same plating solution as in example 1 and the same solution temperature of 170° F., plating of a one-half inch type 1018 steel rod end was carried out at a disc speed of 100 surface feet per minute, a cathode rotation of 40 r.p.m. and a pressure of 25 p.s.i. of the cathode face against the mesh disc. The electrolyte flow was at the rate of 2.0 gal./min. With a current density of 2,160 amps per square foot, a thick, adherent, bright, inclusion-free deposit of nickel was obtained. The thickness of the deposit was 3.25 mils after 5 minutes of plating.

EXAMPLE 3

Using exactly the same arrangement and conditions as in example 2 but reducing the disc speed of rotation to 10 surface feet per minute, gave an electrodeposit which was of comparable thickness and compactness but which was less bright than that obtained according to example 2. Varying the pressure to 5 p.s.i. and to 10 p.s.i. gave essentially the same results as the 25 p.s.i. pressure. Retaining the conditions of example 2 but increasing the disc speed to 1,000 surface feet per minute and the current density to 8,080 amps per square foot gave a compact, smooth and bright nickel deposit of 0.56 mils thickness in 5 minutes.

EXAMPLE 4

Using the apparatus illustrated in FIG. 3 and the same type of activating disc as in example 2, except that it was dulled for 11 minutes by running under 20 p.s.i. against a 304 stainless steel surface at 299 surface feet per minute, a type 1018 steel workpiece one-half inch in diameter was plated from a solution of 13.3 oz./gal. $SnSO_4$ and 13.3 oz./gal. H_2SO_4. The workpiece was the cathode and a lead plate the anode. Electrolyte flow was at the rate of 2.0 gal./min. The anode and associated activating disc was rotated at 10 surface feet per minute while the cathode was rotated at 40 r.p.m. Pressure of the cathode on the disc was 25 p.s.i. Plating was carried out at room temperature and with a current density of 7,200 amps per square foot for a period of 4 minutes, producing an adherent, compact, smooth tin plate of 1.26 mils thickness. (As far as can be found in the literature, tin has not previously been plated from this solution in other than dendritic form even at low current densities.)

EXAMPLE 5

Using the apparatus of FIG. 4, a leaching solution of 42 g./l. copper and 175 g./l. free sulfuric acid was prepared. The rotating disc anode was composed of lead containing about 15 percent antimony. The porous activating disc was the same as that described in example 1. The anode was then rotated and copper deposited out on the cathode which was composed of sheet copper. Sufficient pressure was maintained between the activating disc and the electrodeposit to produce faint scratches visible to the unaided eye. The rate of copper deposition exceeded by many times the rate achieved in the absence of the activating medium.

EXAMPLE 6

Using the apparatus of FIG. 3, an activating disc was made up from 10×10 mesh/in.^{2} glass fiber screen coated with particles of phenolic resin and cured for 24 hours at 300° F. The Knoop hardness of the resin was 40. With the anode again a lead plate rotating at 7,500 surface feet per minute, an electrolyte solution of 13.3 oz./gal. $SnSO_4$ and 13.3 oz./gal. H_2SO_4 was fed at the rate of 2.0 gal./min. onto the resin coated disc mounted on the face of the lead anode. The cathode was a one-half inch diameter 1018 steel rod rotated at 40 r.p.m. and pressed against the mesh disc with a pressure of 25 p.s.i. Plating was carried out at room temperature and with a current density of 11,000 amps per square foot. The resultant plate achieved over a 5 minute period was a very bright, compact, adherent tin plate exceeding 16 mils in thickness.

EXAMPLE 7

Following the identical conditions of example 2 except substituting for the activating disc a 21×20 mesh/in.^{2}, leno weave nylon fabric evenly coated with a smooth phenolic resin coat-

ing containing no particulate material, it was found that the plate produced was very thin, burnt, dendritic and nonadherent. The only difference between this run and that of example 2 was the lack, in this instance, of any activating particles indicating the necessity of these to the success of this apparatus.

EXAMPLE 8

Using the apparatus setup of FIG. 5, a cylindrical nickel liner was formed. The mandrel was stainless steel to which had been flash-plated by conventional methods a very thin uniform nickel coating. Using the material of example 1 except that the resin coating now contained closely spaced grit 400 aluminum oxide particles, a layer was adhered to the inside of a split ring perforated lead sheet. This anode sheet and associated activating material was stationary while the mandrel (cathode) was rotated inside of the ring and in contact with the activating medium. A deposit of nickel approximately 50 mils in thickness was built up at a rate better than 50 times the rate of deposit from a conventional bath. The current flow was discontinued and a smooth, uniform, dense cylinder of nickel was removed from the mandrel.

EXAMPLE 9

Using the apparatus of FIG. 3, a concentrated electrolyte solution of $AlCl_3$ (containing 5 pounds per gallon $AlCl_3$) was used to plate a brass cathode of one-half inch diameter. The activating disc was similar to that described in example 6 and was again mounted on a lead anode. The anode was rotated at 299 surface feet per minute with a pressure on the mesh disc by the cathode of 25 p.s.i. Plating was carried out for 5 minutes at room temperature and with a current density of 17,500 amps per square foot. At the end of this test, the plated end of the brass rod was coated with a thin white metallic deposit which gave the qualitative test for aluminum by the alizarin lake spot test.

EXAMPLE 10

An impure copper ingot containing about 96 percent copper was shaped into a rectangular form and used as the anode in the nonwoven illustrated in FIG. 6. The activating medium was a nonwoven web of about one-sixteenth inch thickness containing grit 400 aluminum oxide particles bonded thereto by a resin adhesive. The web was laminated on each side of a 20×20 mesh nylon reinforcing fabric to form a continuous belt approximately 6 inches wide. This was run between the anode and a copper cathode. The entire unit was submerged in a copper sulfate solution and a high purity sound copper deposit was formed on the cathode.

The present invention is applicable to the electrodeposition of all metals conventionally deposited. It appears particularly of interest in the electrodeposition of Ni, Cu, Sn and Al from aqueous solutions. However, the electrolyte system may be a nonaqueous, low boiling type, if so desired. The type of movement of the activating media over the surface of the cathode may be varied widely, i.e., it may be linear as well as rotative; it may be a combination of movements, e.g., a rotating device which is also oscillated as it rotates, etc. The only requirement is that there be means to provide relative motion between the two of the order of magnitude herein described. Likewise, this relative movement can obviously be achieved with a moving cathode and stationary activating media or a combination of movements of both. While generally illustrated in connection with an insoluble anode, a soluble anode may be used as is illustrated in FIG. 6 and described in example 10. This is particularly desirable in electrorefining operations and simultaneous wiping of the anode and electrodeposit surface with the activating medium has proven valuable. Activation of the anode has been found to increase the rate of anode dissolution and to prevent the buildup of anode slimes, particularly in the refining of tin. In some instances, activation of the anode alone or at a differential rate by the use of this apparatus may be desirable.

The activating media described herein may likewise be varied widely, both in shape or configuration and in composition. The requirements of the supporting members and associated dynamically hard particulate materials has been discussed in detail above. Any nonconductive fibrous material capable of resisting erosion by the electrolyte and capable of producing the described supporting matrix may be used for the porous matrix as well as nonfibrous material such as sponge, foam, or the like. As indicated above, the matrix may be nonporous, if desired, especially where it is desirable to minimize the spacing between the anode and the cathode. The nonconductive particulate activating materials likewise are noncritical in that many materials such as resin particles, abrasive grain, ceramic particles, glass particles, walnut shells or the like can be utilized.

The electrolyte is preferably held at ambient or room temperature, e.g., 20° C., but can be used at temperatures up to the boiling point of the respective electrolyte used in a given setup.

Electrode spacing can vary from as little as one mil up to an electrode gap distance fixed only by the IR drop considered acceptable for the particular operation.

The pressure of the activating medium on the electrodeposit surface, which as indicated above is variable depending on the particular activating particle used and the system in which it is used, may either be held relatively constant throughout any given deposition operation or varied, as desired, during the operation within the limits set by the requirement of the development of the aforementioned scratch pattern and the practical limit set by removal of undue amounts of metal.

We claim:

1. Apparatus for the high speed electrodeposition at high current densities of a smooth, dense, compact metal deposit onto a substrate which comprises:
   a. spaced electrode means constituting at least one anode, and at least one cathode;
   b. means to supply an electrolyte between said spaced electrode means at a high flow rate;
   c. a supporting means having a plurality of spaced hard particles thereon interposed between said spaced electrolyte means with said particles in contact under pressure with at least a surface of said cathode;
   d. means for establishing relative motion and contact between said cathode surface and the particles supported by said supporting means;
   e. means to initiate an electrodeposition current flow through said electrolyte and said supporting means between said anode and said cathode whereby an electrodeposit forms on said cathode surface; and
   f. means for continuing said relative motion during the period of electrodeposition current flow whereby contact of said particles on said supporting means with said electrodeposit is repeated at extremely short time intervals and the surface of said electrodeposit is thereby mechanically activated throughout the entire electrodeposition period.

2. Apparatus as in claim 1 wherein said supporting means comprises an electrolyte-permeable matrix having a plurality of small particles adhered thereto in fixed spaced relationship one to the other.

3. Apparatus as in claim 2 wherein said matrix comprises a porous nonwoven web.

4. Apparatus as in claim 2 wherein said matrix comprises an open-weave fabric.

5. Apparatus as in claim 1 wherein means is provided to continuously move said supporting means relative to said cathode surface.

6. Apparatus as in claim 1 wherein said particles have a dynamic hardness sufficient to produce a scratch in said electrodeposit visible under magnification of 10,000 power.

7. Apparatus as in claim 1 wherein said particles comprise abrasive grains.

8. Apparatus as in claim 1 wherein said supporting means functions as said electrolyte supply means to carry fresh elec-

trolyte into contact with the mechanically activated surface of said electrodeposit.

9. In an apparatus for electrodeposition wherein an electrodeposit is formed on a cathode surface the improvement which comprises:

a. an activating means, having a plurality of nonconductive hard particles supported by and affixed to a matrix, in contact with the surface of said electrodeposit; and

b. means to move said activating means in contact with and relative to said electrodeposit surface throughout the period of said electrodeposition.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,619,401 Dated November 9, 1971

Inventor(s) Steve Eisner

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Patented "Nov. 9, 1917" should read --Nov. 9, 1971--.

Col. 1, line 60, change the word "processed" to --processes--.

Col. 1, line 62, change the word "or" to --of--.

Col. 1, line 70, change the word "activating" to --activate--.

Col. 1, line 75, delete the word "and" [second occurrence].

Col. 2, line 39, change "6.1 x 10^{12} to 3.8 x 10^{17}" to --6.1 x 10^{-2} to 3.8 x 10^{-7}--.

Col. 2, line 67, before the word "illustrative" insert the word --is--.

Col. 2, line 71, change the word "illustrated" to --illustrates--.

Col. 3, line 23, change the word "centimeter" to --centimeters--.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,619,401 Dated November 9, 1971

Inventor(s) Steve Eisner

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 3, line 47, after the word "pressure" and before the word "to" insert the following --applied through the apparatus to the activating means but in order to insure adequate activation of the surface it is usually desirable to apply sufficient pressure--.

Col. 3, line 66, change "1.25 x 10^{11} inches to 5.65 x 10^{14}" to --1.25 x 10^{-1} inches to 5.65 x 10^{-4}--.

Col. 4, line 6, change "1 x 10^{15} inches to 1.25 x 10^{11}" to --1 x 10^{-5} inches to 1.25 x 10^{-1}--.

Col. 4, line 8, change "9 x 10^{14} inches to 2 x 10^{12}" to --9 x 10^{-4} inches to 2 x 10^{-2}--.

Col. 5, line 2, change the word "electrolyteipassing" to --electrolyte-passing--.

Col. 7, line 61, after the "," insert the words --leno weave,--.

Col. 9, line 43, change the word "nonwoven" to --apparatus--.

Col. 10, line 40, change the word "electrolyte" to --electrode--.

Signed and sealed this 9th day of May 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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