United States Patent

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[72] Inventor **Steve Eisner**
Schenectady, N.Y.

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[73] Assignee **Norton Company**
Troy, Mass.
Continuation-in-part of application Ser. No. 718,468, Apr. 3, 1968, now abandoned.

[54] **ELECTRODEPOSITION**
17 Claims, 8 Drawing Figs.

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[51] **Int. Cl.** **C23b 5/50,** C23b 3/06, C23b 5/50
[50] **Field of Search** 204/14, 29, 35, 36, 106, 280, 225–226, 200, 203, 207, 208, 209, 215, 283, 224

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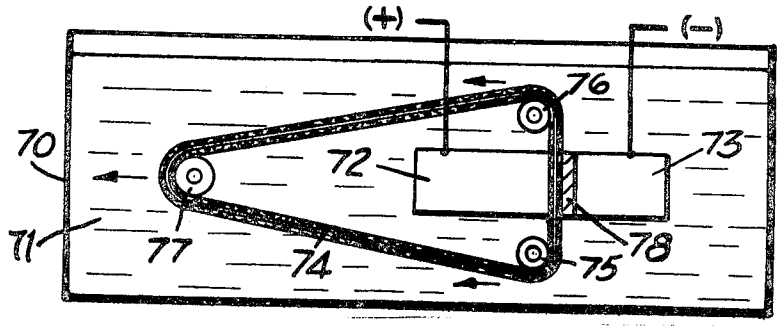
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Primary Examiner—John H. Mack
Assistant Examiner—R. J. Fay
Attorneys—Hugh E. Smith and Herbert L. Gatewood

ABSTRACT: An activating medium comprising a matrix containing small, dynamically hard particles held in spaced fixed relationship to one another is continuously moved under pressure against a surface being subjected to electrodeposition of metal from aqueous or low boiling electrolytes. The dynamically hard particles repetitively contact the electrodeposit at extremely short time intervals generating new surface defect sites and increasing the areas available for nucleation, allowing the use of very high current densities and a consequent rapid rate of dense, compact metal deposition. The matrix may also serve to feed fresh electrolyte to the surface being plated thereby insuring an adequate supply of metal ions required for the rapid plating action.



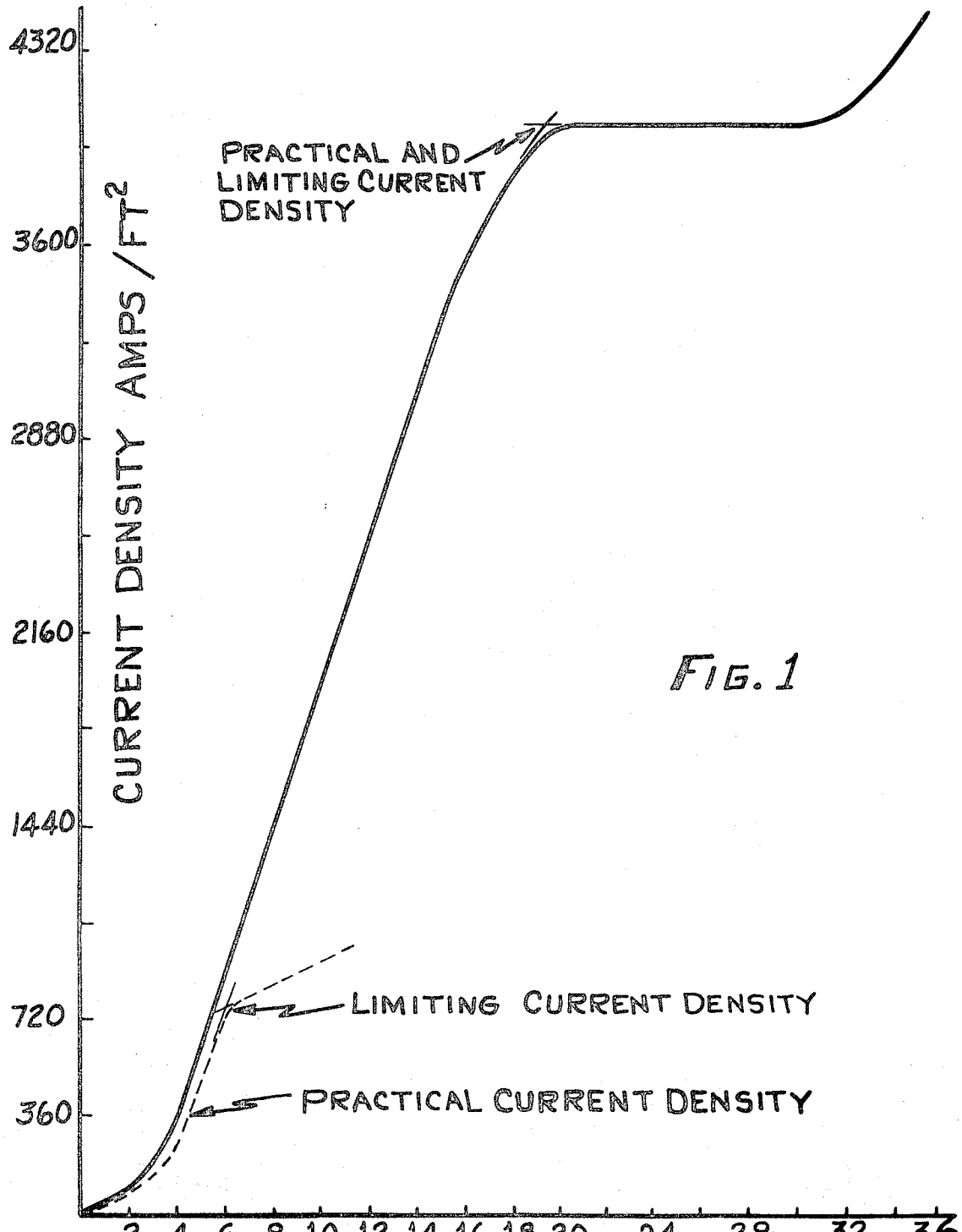


FIG. 1

INVENTOR
STEVE EISNER
BY Hugh E. Smith
ATTORNEY

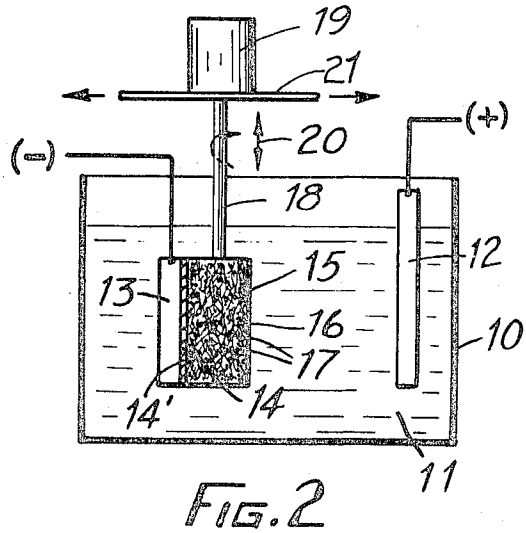


FIG. 2

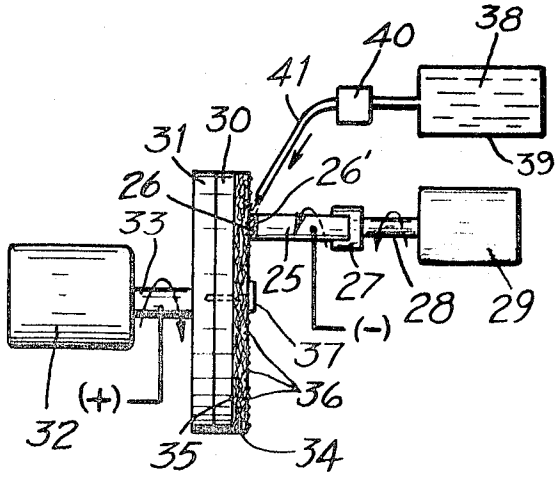


FIG. 3

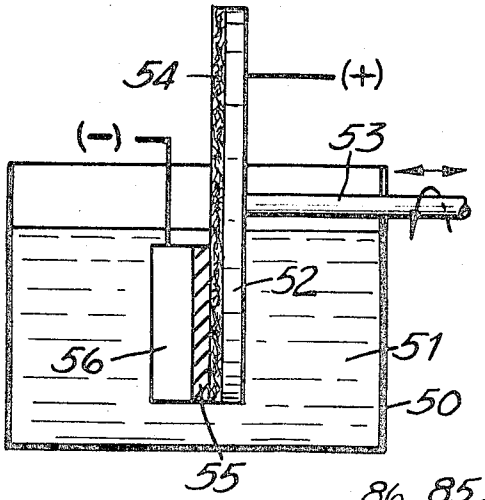


FIG. 4

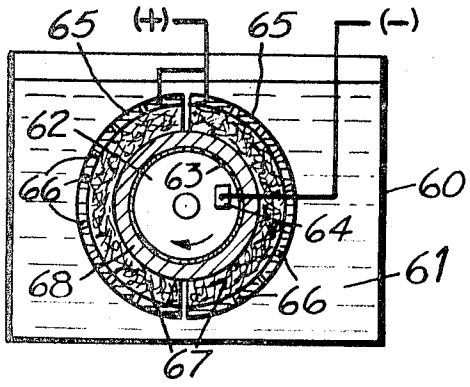
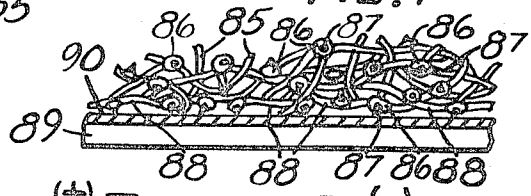


FIG. 5

FIG. 7



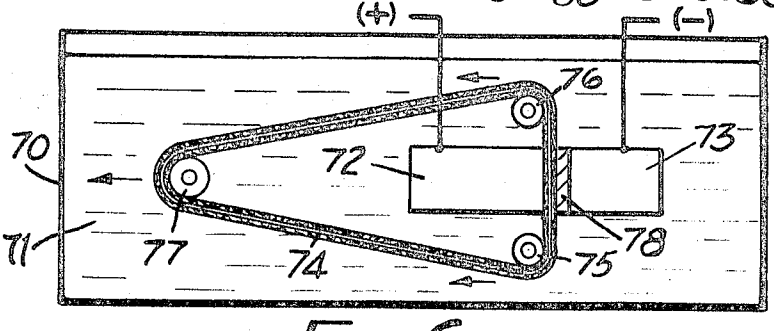


FIG. 6

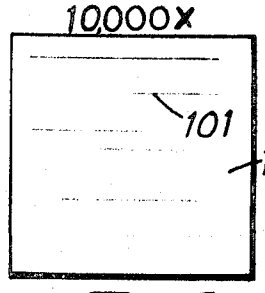


FIG. 8

INVENTOR
STEVE EISNER
BY Hugh E. Smith
ATTORNEY

ELECTRODEPOSITION

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of my earlier filed application, Ser. No. 718,468, filed Apr. 3, 1968 (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 depositing sound, coherent plates from 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.

SUMMARY

The present invention is directed towards a process in which the current density is high compared with that of conventional processes, e.g., 20,000 amps per square foot vs. 1,000 amps per square foot for conventional tin plating, and in which the surface of the deposit is 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 "activate" the surface. "Activating" the surface of the electrodeposit within the meaning of the present invention means so treating the surface as to create at such surface a high tendency to utilize the current to deposit the metal in sound, adherent form rather than as powder or dendrites. It is believed that the mechanism is rather complex and consists of several actions taking place essentially simultaneously. Among others, there appears to be new surface defect site generation resulting from distortion of the crystal lattice structure. 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 process requires the use of a surface disturbing or activating medium having the characteristics of 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 which also provides a plurality of liquid entrapping or sweeping members extending parallel with and closely adjacent to the surface being plated. The process further requires relative motion during the deposition operation between the surface receiving the deposit and the activating medium. In addition, sufficient pressure is applied to said activating medium 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 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^{-2} to 3.8×10^{-7} seconds. Fresh electrolyte is supplied to the zones of activated metal deposit at the same rate through entrapment by the liquid entrapping or sweeping members of the activating medium (which members may be the edges of the particles) parallel with the electrodeposit surface. These members sweep fresh electrolyte along with them, the electrolyte reaching such members due to the porosity of the supporting matrix of the activating medium or through proper disposition of the electrolyte supply adjacent the contact area between the activating medium and the electrodeposit surface.

Accordingly, the principal object of the present invention is the provision of a high speed electrodeposition process 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 graphically the increase in limiting current density achieved with the process of the present invention.

FIG. 2 is a schematic illustration of the process 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 the present process as applied to such an arrangement.

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

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

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

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

FIG. 8 is a photomicrograph of the coating plated on a surface by the apparatus and method illustrated in FIG. 2 hereof, illustrating the typical scratch pattern visible with the naked eye or under magnifications of up to 10,000 power.

DESCRIPTION OF PREFERRED EMBODIMENTS

The process of the present invention requires the controlled application under pressure to the surface of the electrodeposit of a supporting, preferably porous, matrix which supports in closely spaced relationship a plurality of small, relatively inflexible particles. These particles are so positioned in the matrix as to contact the deposit forming on the cathode surface and relative motion between such particles and the deposit must be maintained during electrodeposition. 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 centimeters. Under application of the supporting matrix and associated particles according to the present invention, this polarization layer is repetitively removed or its thickness substantially diminished repetitively throughout the plating cycle. As described above, the process activates the electrodeposit surface by apparently 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.

This technique has been found to increase the limiting current density many times beyond that possible with other methods, resulting in much more rapid sound metal deposition than is possible with such other methods. The present method has further been found to produce a hard, dense, smooth metal deposit. These results are achieved even though practical application of the process 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 applied to the activating medium but in order to insure adequate "activation" of the surface it is necessary to apply sufficient pressure to produce a light scratch pattern in the metal deposit. Thus the dynamic hardness of the particles may be substantially greater 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, nonconductive 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 nonrandom 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 and are believed to knock down or cut off if 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 10,000X magnification.

The most graphic effect of the present process 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. As illustrated in FIG. 1 of the drawings, this curve will turn up 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). In the present process, not only is the limiting current density also the practical current density, but such current density is substantially above the limiting current density for conventional processes. Referring to FIG. 1, a plot of current density vs. voltage is shown. The lower curve shown in dotted lines is the plot of current density vs. voltage for an electroplating system for nickel using conventional techniques. Using exactly the same system but incorporating the activating process of the present invention results in the solid line curve shown in FIG. 1. It is apparent that the present process which gives both a practical and a limiting current density at 4,020 amps/ft.^{2} is far above the practical current density of 385 amps/ft.^{2} and the limiting current density of 792 amps/ft.^{2} of the conventional process. In this illustration, the activating medium was 20×20 mesh per inch treated rayon fabric carrying resin-bonded grit 400 aluminum oxide as the activating particles. The activating medium was run at a speed of 1,000 surface feet per minute relative to the electrodeposit and under a normal pressure of 25 p.s.i.

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 2-¼-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 preferably has a plurality of thin-walled members extending between the activating particles to act as electrolyte sweeps. While these members may be the edges of the particles themselves, in the preferred embodiments these thin-walled members are formed by the porous matrix and 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 the present process by making it

nonconducting, i.e., it essentially becomes a standard coated abrasive product with electrolyte-passing 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 in the present process must have as the conductive layer of metal an inert-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. patent, U.S. 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. Additionally, the matrix may be in particulate form, e.g. spheres, with a plurality of dynamically hard particles adhered to or protruding from the surface thereof in spaced relationship to one another.

Referring again to the drawings, FIG. 2 is a schematic plan view of the process 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 is an anode 12 and a cathode 13 connected to a conventional power source. 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 driven 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 face 14 of the cathode 13 by the activating drum 15. Rotation of the drum 15 against the face 14 of cathode 13 causes the previously described activation of the electrodeposited layer 14' which builds up on face 14. This rotation 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 apparatus for practicing the present invention without actual immersion in a bath. 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 conventional power supply (not shown) and is mounted for rotation in a chuck 27 at the end of a shaft 28 of a conventional 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 the present process used in electrowinning copper from a leaching solution of copper and sulfuric acid. The system 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. 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 process to the electroforming of a particular shape—in this instance a cylinder. The system 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 (not shown). 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 medium 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 process as applied to the electrorefining of an impure metal. The system 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. A cathode 73 of the metal to be deposited is in contact with the other side of belt 74 initially, but at the point in the deposition cycle illustrated in FIG. 6, the belt 74 is 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 herein elsewhere 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 process they would be in contact therewith.)

FIG. 8 illustrates a photomicrograph of a plated cathode face produced by the method of the present invention. In this instance, oscillation of the activating media did not take place and the scratch pattern 101 in the plated surface 102 extends in the direction of relative movement between the cathode face and the activating media. The existence of scratches in

the plated surface visible under a magnification of 10,000X is characteristic of the plate produced according to the present method. These scratches are usually so minute as to not be objectionable and do not adversely affect the commercial quality of the plate for most purposes. If desired, conventional plating processes can be employed to cover the surface of the deposit produced by the present process to minimize or eliminate such surface scratches.

The following specific examples are furnished for the purpose of illustration of some of the variations possible with the present method:

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 two 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-quarter 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 rotated while a jet of electrolyte formed from a mixture of 49.5 oz./gal. of $NiSO_4 \cdot 6H_20$ 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 under 25 p.s.i. pressure. This rod was connected to the power supply as the cathode. 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}, leno weave, 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 seven 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 ½-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 moderate pressure of the cathode face against the mesh disc sufficient to produce light scratches in the surface of the plate formed. 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. 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 20 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 sufficient to produce faint scratches visible to the unaided eye. 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

A porous activator was made by first needle-punching a nonwoven web of 3-denier polyester fibers (multiple equispaced barbed needles were pushed through normal to the plane of the web and forced fibers caught by the barbs through the web to mechanically interlock the fibers). The web had an average weight of 175 grams/yd.^{2} and was approximately 0.1 inches thick. The needle-punched web was then roll-impregnated with a curable urethane emulsion (40 percent solids) containing 600 grit silicon carbide abrasive particles. This slurry consisted of 70 percent urethane emulsion and 30 percent abrasive grain by weight. The deposited weight of impregnant was 14 pounds per sandpaper ream. The impregnated web was air dried at 50 percent relative humidity and 70° F. for 1 hour and then air cured at 250° F. for 5 hours.

A 9-inch diameter disc of this material was died out and provided with a ⅞-inch diameter center hole. This disc was then clamped firmly to the surface of a 9-inch diameter rotatable copper sheet anode supported on a driven wheel member. A 2-inch diameter stainless steel disc was utilized as the cathode and was placed against the surface of the rotating activator disc so that the center of the cathode disc was about 3 inches from the center point of the activator disc. A pressure of 0.035 p.s.i. was used to hold the cathode disc against the activator surface.

A solution of 300 gm./l. $CuSO_4 \cdot 5H_20$ plus 100 gm./l. H_2SO_4 was then continuously sprayed against the activator pad at the point where it contacted the cathode disc. The activator disc was rotated at a surface speed of 50 surface feet per minute

measured at 3 inches from the center of such disc. A current density of 200 amps per square foot was then maintained at the cathode and a sound copper deposit was laid down on the surface of the cathode. Due to the stainless surface of the cathode, the copper layer was readily peeled off as a coherent sound sheet.

EXAMPLE 7

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 ½-inch diameter 1018 steel rod rotated at 40 r.p.m. and was pressed lightly against the mesh disc. 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 8

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 coating 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 process.

EXAMPLE 9

Using the apparatus setup of FIG. 5, a cylindrical nickel liner was formed. The mandrel was stainless steel to which had been flash-plated 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 10

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 7 and was again mounted on a lead anode. The anode was rotated at 299 surface feet per minute with a light pressure on the mesh disc by the cathode. 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 11

An impure copper ingot containing about 96 percent copper was shaped into a rectangular form and used as the anode in the system 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.

EXAMPLE 12

Using the same activating material, electrolyte solution and equipment setup described in example6, the activator disc was rotated at a speed of 100 surface feet per minute (at the cathode) and a current density of 500 amps per square foot was imposed. Here a pressure of 0.14 p.s.i. was used and a sound copper deposit was obtained. Under exactly the same conditions but utilizing as the activator disc an identical material except for the omission of any hard particles, the only deposit which could be obtained was powdery and noncoherent.

EXAMPLE 13

Again using the activating material, electrolyte solution and equipment setup of example 6, but increasing the activator disc speed to 400 surface feet per minute and the pressure applied on the activator to 0.2 p.s.i., a sound copper deposit was achieved on the cathode at a current density of 1,500 amps per square foot.

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 relative motion between the two of the order of magnitude herein described and claimed. 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 11. 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 this process 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. Pressures from as low as 0.035 p.s.i. up to 25 p.s.i. have been used. Generally, pressures in the range of from 0.1 to 0.5 p.s.i. are sufficient to produce the desired scratch formation and are usually preferred.

I claim:

1. A process for the high speed electrodeposition at a high current density of a smooth, dense, compact metal deposit onto a substrate, the improvement which comprises: discontinuously activating the entire surface of the electrodeposit at extremely short repetitive time intervals throughout the period of imposed current flow by contact between such surface and a plurality of small activating particles held in spaced relationship to one another on a supporting matrix which is mechanically moved relative to such surface and, coincident with such mechanical activation, supplying quantities of fresh electrolyte at a high flow rate to such surface.

2. A process as in claim 1 wherein the extremely short time intervals are not more than 6.1×10^{12} seconds.

3. A process as in claim 2 wherein the matrix is electrolyte permeable.

4. A process as in claim 2 wherein the activating particles have a dynamic hardness sufficient to produce a scratch in said electrodeposit visible under magnification of 10,000 power.

5. A process as in claim 2 wherein the matrix functions to carry quantities of fresh electrolyte over the surface of the electrodeposit with which it is in contact.

6. A process as in claim 1 wherein the electrodeposition takes place within an electrolyte bath.

7. A process as in claim 2 wherein the electrolyte is fed into the interface between said electrodeposit and said matrix.

8. A process as in claim 1 wherein said high current density is in excess of the current density achievable in the absence of mechanical activation of the surface of the electrodeposit.

9. A process as in claim 4 wherein the pressure between said particles and the surface of said electrodeposit is in the range of 0.035 to 25 pounds per square inch.

10. A process as in claim 9 wherein the particle size ranges from 1.0×10^{15} to 1.25×10^{11} inches and such particles have a minimum Knoop hardness of 10.

11. A process for the high speed electrodeposition at high current densities of a smooth, dense, compact metal deposit onto a substrate which comprises:

a. establishing a system having an anode, a cathode and an electrolyte therebetween;

b. interposing between said anode and said cathode in contact under pressure with at least a surface of said cathode a matrix having at least on its surface a plurality of spaced activating particles secured in spaced relationship to one another;

c. establishing relative motion between said matrix and said cathode surface whereby electrolyte is moved at a high flow rate across said cathode surface;

d. initiating an electrodeposition current flow through said electrolyte and said supporting matrix between said anode and said cathode whereby an electrodeposit forms on said cathode surface; and establishing relative motion and contact between said electrodeposit on said cathode surface and the particles supported by said medium whereby said surface of said electrodeposit is mechanically activated;

e. continuing said relative motion during the entire period of electrodeposition current flow whereby contact of said particles supported by said matrix with said electrodeposit is repeated at extremely short intervals and the surface of said electrodeposit is thereby mechanically activated throughout the entire electrodeposition period.

12. A process as in claim 11 wherein said supporting matrix comprises an electrolyte-permeable material.

13. A process as in claim 12 wherein said matrix comprises a porous nonwoven web.

14. A process as in claim 12 wherein said matrix comprises an open-weave fabric.

15. A process as in claim 11 wherein said extremely short time intervals are less than 6.1×10^{12} seconds.

16. A process as in claim 11 wherein said particles have a dynamic hardness sufficient to produce a scratch in said electrodeposit visible under magnification of 10,000 power.

17. A process as in claim 11 wherein said particles comprise abrasive grains.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,619,384 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. 1, line 45, after "vs." insert the word --around--.

Col. 2, line 22, change "6.1 x 10^{1a2} to 3.8 x 10^{17}" to read --6.1 x 10^{-2} to 3.8 x 10^{-7}--.

Col. 3, line 51, change "1.25 x 10^{11} inches to 5.65 x 10^{14}" to read --1.25 x 10^{-1} inches to 5.65 x 10^{-4}--.

Col. 3, line 64, change "1 x 10^{15}" to read --1 x 10^{-5}--.

Col. 3, line 65, change "1.25 x 10^{11}" to read --1.25 x 10^{-1}--.

Col. 3, line 66, change "9 x 10^{14}" to read --9 x 10^{-4}--.

Col. 3, line 67, change "2 x 10^{12}" to read --2 x 10^{-2}--.

Col. 11, line 11, before the word "A" insert --In--.

Col. 11, line 23, change "6.1 x 10^{12}" to read --6.1 x 10^{-2}--.

Col. 12, line 1, change "1.0 x 10^{15} to 1.25 x 10^{11}" to read --1.0 x 10^{-5} to 1.25 x 10^{-1}--.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,619,384 Dated November 9, 1971

Inventor(x) 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. 12, line 19, after "and" delete the words --establishing relative motion--.

Delete lines 20 thru 23.

Col. 12, line 27, after "short" insert the word --time--.

Col. 12, line 37, change "6.1×10^{12}" to read --6.1×10^{-2}--.

Signed and sealed this 18th day of April 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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