ABSTRACT OF THE DISCLOSURE

A process and apparatus for simultaneously and uniformly plating numerous particles of small diameter. The apparatus comprises a column containing plating solution flowing vertically therethrough. Upper and lower transverse screens border the inside dimensions of the column interior of the plating solution and therewithin confine the particles being plated. Vibrational energy in the range of 20 cycles per second imparted to the plating solution strips the particles being plated of the gaseous by-products of plating thereby preventing gas binding of the plating reaction. Plating solution as vertically flowing through the plating segment moves those particles having low plating size and density into zones of the segment where plating occurs and permits those particles having the desired plating deposit thereon to settle into zones of the segment where plating is arrested.

This invention relates to metal plating and more specifically sets forth an apparatus for simultaneously and uniformly plating numerous particles of small dimension.

The plating of particles having dimensions smaller than 1,000 microns has in the past been limited because of gas binding produced within the plating solution. Typically, the plating reaction produces various gaseous by-products. These gaseous by-products accumulate on the particle surfaces being plated and insulate such surfaces from contact with the plating solution, thereby preventing the plating reaction from occurring. This insulation or gas binding of the surfaces being plated produces a non-homogeneous plating deposit on the particles. The apparatus of the instant invention prevents gas binding from occurring by purging or wiping the accumulation of the gaseous by-products on the particle surfaces and thus enables particles as small as 10 microns to be homogeneously plated.

The disclosed plating apparatus comprises a column defining a cylindrical interior of circular cross-section which interior contains a plating solution. This column has upper and lower insulating screens contacting the inside diameter of the column, confining the particles being plated therewithin to a plating segment of the column within the plating solution. The screen at the upper extremity of the bath is mounted for vibrational movement interior of the column and has vibrational energy in the range of 20 to 20,000 cycles per second imparted thereto. This vibrational energy is transmitted from the screen to the plating solution and particles being plated. The imparted vibrational energy strips the gaseous by-products of the plating reaction from the interfaces between the particle surfaces and plating solution preventing gas binding of the desired plating reaction.

This screens defining a plating segment interior of the bath permit a continuous flow of plating liquid therethrough. Such flow permits the plating solution in the plating segment to be replenished and furthermore permits the plating fluid to be flushed from the plating zone when the particles being plated have contained thereon the required amount of plating material.

Regarding the flow of fluid through the plating zone, such flow is achieved by adding the plating liquid to the column at one end and removing fluid from the column at the other end. Such addition and removal of plating fluid produces a vertical flow in the plating segment of the column. This vertical flow may be utilized to assure that each particle inserted within the plating segment has uniform amounts of plating material deposited thereon, and to precisely control the size to which each batch or group of particles is plated.

Regarding the uniformity of the particles within each group or batch as plated, the plating segment of the column is divided into an upper plating zone where plating reaction occurs and into a lower zone wherein the plating reaction is retarded.

During the plating process particles having less than the desired plating deposit contained thereon and therefore being of relatively low size and density are entrapped and entrained in the flow of plating solution. These particles move from the lower non-plating zone to the upper zone where plating occurs. Conversely, particles having deposited thereon the desired plating deposit contained thereon and therefore being of relatively large size and density gravitationally settle against the flow of plating solution. These settling particles move from the upper plating zone to the lower zone of the plating segment where the plating is arrested.

This same upward flow of plating solution through the plating segment of the bath may be utilized to precisely control the size and density of each batch or group of particles plated interior of the column. Typically, it will be desired to plate uniformly sized particles with precise amounts of plating material thereon so as to assure the same particle density and size between sequential groups or batches within the reactor. Such control over the density and size can be achieved in the present invention by adjusting the upflow of the plating solution through the plating segment of the bath. As adjusted, the solution velocity may be maintained at a level where particles below a certain size and density will be supported within the plating zone of the bath while those particles having achieved the requisite size and density through plating will settle into the non-plating zone of the bath thereby preventing further deposit of the plated material.

Other objects, features and advantages of the present invention will be more apparent after referring to the following specification and attached drawing in which:

FIG. 1 is a plating reactor system specifically illustrating in section a plating column having a mounted vibrational screen for imparting vibrational energy to the plating segment of the column and;

FIG. 2 is a column having a plurality of plating segments defined therein for plating simultaneously separated batches of particles with the same column.

With reference to FIG. 1, column A containing a plating solution B is shown. Interior of the column and within the plating solution B there is defined a plating segment C. Segment C extends between a lower stationary screen D and an upper vibrational screen E. This segment confines particles F to be plated with plating solution B.

Regarding the plating of particles F, these particles are inserted interior of the column A at the plating segment C. When the particles are inserted, vibrational energy in the range of 20 to 20,000 cycles per second is imparted to upper vibrational screen E. Screen E in turn imparts its vibrational energy to plating solution B and particles F. As vibrated, plating solution B and particles F are prevented from having the gaseous by-products of the plating reaction formed on the interface between the particles and plating solution thereby permitting homogeneous plating to occur.

Column A comprises a hollow elongate glass cylinder which cylinder defines a horizontal cross-section cir-
circular in shape. Cylinder 14 has fastened at either end thereof bottom plate 15 and top plate 16 which plates seal the interior volume of column A so that it may contain plating solution B.

Plating solution B is a solution having the metallic atoms being plated in ionic suspension. As the present invention is applicable to processes wherein electro-plating occurs with and without the presence of a current field, plating solution B can be virtually any known solution wherein the ionically suspended metallic atoms can be taken out of solution and deposited upon particles F within the solution.

Interior of plating solution B there is defined a plating segment C. Segment C has for its boundaries the interior side walls 18 of cylinder 14, lower stationary screen D and upper vibrating screen E. This segment C is wholly within plating solution B and functions to keep particles F immersed so as to assure their contact with the plating solution.

A preferred embodiment of the present invention would include particles F comprising polymeric beads formed from polystyrene cross-linked with divinyl benzene. Such beads have sulfonate groups bonded to the outside thereof and are immersed in a suitable solution for plating metallic atoms on the particle surfaces. A plating solution B for electrosol bonding of copper atoms to such beads would be:

- Copper nitrate—15 g./l.
- Sodium bicarbonate—10 g./l.
- Rochelle salt—30 g./l.
- Sodium hydroxide—20 g./l.
- Formaldehyde (37%)—100 ml./l.
- pH—11.5
- Temperature (° F.)—75

Other examples of minute particles capable of being plated with metallic atoms are set forth in co-pending application Ser. No. 613,136 filed Feb. 1, 1967, by James A. Patterson and Robert K. Schonian entitled “Metal-Coated Polymers.”

Particles F when disposed interior of said bath are placed in a spatially separated disposition wherein the particles will not be in contact with one another when plated. Such placement requires that the interstitial void volume between the beads as being plated be greater than 35%.

Screens D and E have a mesh smaller than the largest particles F to be plated. In the present invention, these screens have a nylon mesh which mesh may be as small as 10 microns in diameter. Thus plating segment C may effectively accommodate therein particles F which particles are within the range of 10 microns minimum diameter.

Regarding the plating of particles having dimensions of 1,000 microns or lower, present plating equipment is unable to effectively plate particles of this dimension because of the gas binding of the particles being plated. This gas binding is produced by gaseous by-products forming at the interface between the particles being plated and the plating solution. These gaseous by-products as formed randomly accumulate on the particles being plated and insulate the particle surfaces from the plating solution. This random accumulation and insulation produces a non-uniform plating of minute particles F.

The prior art has attempted to plate such minute particles by confining the plating solution and particles interior of a rotating barrel. As rotated, the barrel to some degree mixes the particles and plating solution thereby preventing the accumulation of relatively large gas bubbles on the particles. Unfortunately, this removal of gaseous by-products in a rotating barrel is ineffective against gas bubbles of small dimension and particularly fails where the particles are below 1,000 microns in dimension.

The present plating reactor overcomes these limitations of the prior art by having a vibrating screen E. Screen E comprises a screen mount assembly 20 having mounted thereon upper vibrating screen E. Screen mount assembly 20 comprises a hollow cylinder 21 which cylinder has a periphery or outside diameter 23 slightly less than the inside diameter of glass cylinder 14. Configured in the periphery of outside diameter 23 there are seal ring grooves 24, which grooves have contained therein seal rings 25. Rings 25 are disposed interior of groove 24 slightly exceed the inside diameter of cylinder 14 and effect a compressive seal between the inside side wall 18 of column A and periphery of screen mount assembly 20.

Screen E attaches at its periphery to screen mount assembly 20 and covers the open portion 27 thereof. As covering open portion 27, screen E has attached at the central portion thereof a rod 30 which rod imparts vibrational energy to the screen.

Rod 30 fastens to screen E at hole or aperture 29 provided in the central portion of the screen. This rod attaches to the screen at paired screen fasteners 31.

Paired screen fasteners 31 are typically threadably attached to rod 30 on either side of screen E. These fasteners have a periphery which exceeds the diameter of aperture 29 through which rod 30 protrudes. Attachment to screen E is effected by turning fasteners 31 to compress therebetween a portion of screen E immediately adjoining aperture 29. As compressed towards one another, fasteners 31 affix rod 30 to screen E so that the vibrational energy transmitted to the rod may in turn be imparted to the screen.

Rod 30 is provided with vibrational energy by a vibrator 34. Vibrator 34 is typically exterior of column A and attached to the upper extremity of rod 30. Rod 30 extends through plate 16 at the top of cylinder 14 at rod aperture 35. For maintaining the desired pressure within the plating segment, aperture 35 is provided with a fluid tight seal to rod 30. This seal permits vibrational energy to be transmitted from vibrator 34 to screen E without releasing pressures interior of column A.

As utilized for plating particles F the disclosed reactor typically has the top plate 16 and screen E removed. Thereafter, particles F are inserted interior of the column and screen E slideably inserted along the inside walls 18 of the column so as to submerge particles F interior of the plating solution B. Top plate 16 is fastened to the upper portion of cylinder 14 and thereafter the desired plating reaction commences.

When screen E is placed interior of solution B, vibrator 34 imparts vibrational energy to the screen via rod 30. The vibrational energy imparted to screen E in typical within the range of 20 to 20,000 cycles per second. If the vibrational energy is less than 20 cycles per second, the vibration imparted to solution B by screen E will not successfully purge or remove the gaseous by-products from the surfaces of the particles F being plated. Alternatively, if the vibrational energy is greater than 20,000 cycles per second, the vibration imparted to solution B by screen E will remove plating substances deposited on the surfaces of the particles F. As is apparent, solution B or particles F can be vibrated in numerous ways. Accordingly, it will be understood that this invention is not restricted to the particular vibrating apparatus illustrated.

Vibrating screen E imparts vibrational motion to both the solution B and particles F contacting the screen. This vibrational motion strips the particles F of the gaseous by-products of the plating reaction and permits the solution to contact constantly the outside surfaces of the particles so as to produce thereon a constant and homogeneous plating reaction.

Regarding the stripping of the gaseous by-products by the vibrational energy imparted to solution B and particles F, such stripping occurs through movement of particles F and solution B with respect to the formed gaseous by-products. Vibrational energy as imparted to the plating mixture effects minute movement of solution B and particles F. This minute movement causes a vibra-
tional change of position or relative motion of the relatively dense particles and solution as a function of their respective densities. Similarly, the vibrational energy as imparted to the plating mixture also affects minute movement of the gaseous by-products. This minute movement causes a different vibrational change of position or relative motion of the gaseous by-products as a function of the relatively lighter density of the gas. The varying densities of C. particles and solution on one hand and the gaseous by-products on the other hand in causing differing relative movements effectively wipe such gas accumulation from the surfaces being plated.

Additionally, the vibrating screens impart a mixing motion to the particles F and plating solution B keeping a uniform and homogeneous mixture throughout plating segment C.

Vibrating screen E further functions to permit the stripped gaseous by-products to be passed therethrough during the plating reaction. Typically, screens of extremely small mesh tend to confine and prevent gases from flowing therethrough. The outlet 42 receives the lower portion of the screen in bubbles exceeding the dimension of the mesh and thereafter do not pass through the screen. Vibrating screen E through its vibrational motion prevents the collection of gas bubbles on its lower immediately adjoining the lower side of screen E are strained and passed therethrough by the vibrational energy of the screen. As strained and passed through the vibrating screen, the gases pass through the vibrating screen upwardly to the surface of plating solution B.

In addition to each bead having a uniform plating deposit thereon, it has been found that in virtually all practical applications for plated particles the beads must have a uniform size and density with respect to one another. To achieve such uniformity of particle size of plated particles, a plating reactor must satisfy two conditions; the reactor must plate the particles of each batch to a uniform size and density and be capable of plat- ing sequential batches to the same size and density.

Regarding the uniform size and density, plating segment C is typically divided into upper plating zone 48 and lower plating zone 49. These plating zones in combination with vertical flow of plating solution B through the plating segment assure that each batch of particles F is uniformly plated and control the size and density to which the particles of each batch processed within the reactor are plated.

Regarding the vertical flow of plating solution B, column A is provided with an attached plating solution supply G. Supply G in turn is provided with piping for circulating the plating solution or reagents through column B, typically so as to upflow through the plating segment.

Plating supply G comprises a tank 37 containing plating solution 38 together with apparatus for maintaining the plating solution therein at a constant temperature. At the bottom portion of tank 37 there is an outlet 46, which extends into the bottom interior of the tank with the pump 42. Pump 42 has its outlet in turn communicating with piping 43, which piping delivers fluids from the tank directly to the bottom portion of the bath interior of column A. As can be seen in FIG. 1, piping 43 extends through the bottom plate 15 at piping aperture 44.

In order to maintain a constant upflow of plating solution B as the solution is delivered to the bottom of column A, it is necessary that plating solution be removed from the top portion of the column above plating segment C. Accordingly, a plating solution outlet 46 extends through the top plate 16 interior of plating solution B. Outlet 46 extends below top plate 16 a distance where it penetrates the surface of plating solution B. This outlet receives the plating solution under pressure interior of column A and discharges plating solution B interior of tank 37. In order to control the ambient pressure interior of column A, outlet 46 is provided with a pressure control valve 47. Valve 47 regulates the pressure at which plating solution B is discharged into the interior of column A and thereby can control the ambient pressure at which the plating reaction occurs.

Plating segment C of column A is divided into an upper plating section 48 and a lower non-plating section 49. These sections are of their own plating solution B, non-plating solution B, and non-plating solution C that are dependent upon the type of electrolytic plating occurring within plating solution B.

Regarding the specific types of electrolytic plating which can occur within the plating solution B, many plating solution plates particles immersed therein at a zone dependent upon the ambient temperature of the plating solution. In such chemical reactions, upper plating sections 48 may be activated to plate at a relatively rapid rate by heating solution B co-extensively with that portion of column A which zone 48 occupies. In the illustrated example, upflowing plating solution B can be heated by coils 50 co-extensive with plating zone 48 to provide the necessary plating ambient. As will hereinafter become apparent, in the event it is necessary to downflow plating solution B through plating segment C, the plating solution can be cooled co-extensive with non-plating section 49, so as to provide a thermal ambient wherein plating is retained.

Alternatively, other plating solutions B have a plating effect on particles immersed therein, which plating effect is a function of the electric field produced within the plating solution. In such chemical reactions, upper plating section 48 may be activated by paired electrodes 52 and 54. These electrodes are shown in FIG. 1 attached to bottom plate 15 and extending upwardly interior of plating segment C to the bottom portion of upper vibrating screen E. Paired electrodes 52 and 54 each have a lower insulated section 55 co-extensive with non-plating zone 49 and an upper conductive section 56 co-extensive with upper plating zone 48.

The electric field interior of plating segment C is effected by a current source 58 connected across paired electrodes 52 and 56. As is apparent, the desired electric field will be produced between the paired electrodes when the electrical circuit of current source 58 and paired electrodes 52 and 54 is completed through the upper plating zone 48 of plating solution B. As is apparent, the current field produced by the upper conductive section 56 of the paired electrodes will be restricted to upper plating zone 48 and will not occur in that zone of plating segment E which has insulated sections 55 of the respective electrodes.

Assuming that plating segment C has defined therein an upper plating zone 48 and a lower non-plating zone 49, the operation of the disclosed plating reactor to homogeneously plate numerous particles of small dimension may readily be understood.

Assume that numerous particles F have been placed interior of plating segment C and are undergoing a plating reaction. The uniformity of plating of each particle F will be dependent upon the upflow of the plating solution B and the relative size and density of each particle. Further assuming that one particle F has deposited thereon an insufficient amount of plating material. Such an insufficiently plated article will have a size and density less than desired and therefore will tend to be entrapped and entrained within the upflowing plating solution B. Such entrainment will move the insufficiently plated particle from the lower non-plating zone 49 into the upper plating zone 48 wherein plating will occur. Conversely, assume that one particle F has deposited thereon sufficient amounts of plating material. Such a sufficiently plated particle will have a density as desired and will gravitationally settle against the upflow of plating solution B. Such gravitational settling will move the sufficiently plated particle from the upper
It is hereby known that particles suspended within a fluid may be measured according to their size and density by allowing such particles to gravitationally settle against a vertically flowing fluid stream. This phenomenon is referred to as the Stokes effect. This Stokes effect may utilize the present invention to control the size to which particles F of sequential batches inserted interior of the reactor are plated.

Particles F as introduced into the plating solution B have an identical size and density. Plating of such uniform particles can be precisely controlled by adjusting the vertical flow of plating solution B. When relatively dense plating of the particles F is desired, the velocity of plating solution upflow may be increased to a level where relatively dense particles will be maintained within plating segment 48. Alternately, when relatively light plating of the particles is desired, the velocity of plating solution upflow may be reduced to a level where particles having light deposit plating material will gravitationally settle to non-plating segment 49.

Regarding the upflow of plating solution as hereinbefore mentioned must be understood that such upflow is utilized only where the particles as completely plated are of a density exceeding that of solution B. If particles F as plated are of a density lighter than fluid B, it may be desired to reverse or downflow the plating solution between the respective plating and non-plating zones. Such a downflow would cause insufficiently plated particles to buoyantly rise against the downflowing plating solution to upper zone 48 where plating occurs. Conversely, the downflow would cause sufficiently plated particles to lose some of their buoyancy and become entrapped and entrained in one downflowing plating solution to lower zone 49 wherein plating is retarded.

When all particles F have been sufficiently plated, such progress of the disclosed reaction will be readily observable through glass cylinder 14. Particles F when insufficiently plated will typically be grouped or collected in upper zone 48. As the plating reaction progresses, particles F will settle from upper zone 48 where plating occurs to lower zone 49 where plating is retarded. Upon completion of the plating reaction, particles 50 will all be grouped within lower zone 49. This grouping of particles within the lower zone A a condition readily observable through glass column 14 and will signal the operator of the plating reaction to arrest the plating reaction.

Regarding this arresting of the plating reaction, the column A has an advantage not immediately apparent. The plating solution C has defined between screens D and E permits fluids to pass and circulate through the plating segment in an essentially unrestricted basis. This circulation of fluids permits the observed plating reaction to be arrested by flushing the plating fluid from plating segment C when the desired reaction is completed.

To permit such flushing, the disclosed plating reactor is here shown having a flushing inlet 61 controlled by a flushing valve 62. When immediate arresting of the plating reaction is desired, a neutralizing fluid such as water, is introduced through flushing inlet 61 into the interior of column A. Such fluid displaces the plating solution B and immediately arrests any further plating of particles F. By utilizing flushing, inlet 61 and the visible suspension of particles F within plating segment C, the plating reaction may be controlled within precise limits.

Furthtext reacton the plating reaction can be maintained by controlling the rate of plating. This plating rate at which electroplating occurs is controlled by adjusting pressure control valves 47 to vary the ambient pressure of the plating reaction interior of column A.

Regarding the rate of electroplating, most forward chemical plating reactions have a rate of plating dependent upon the speed with which the gaseous by-products of the plating reaction can be permitted to escape. Such escape of the gaseous by-products occurs only when the pressure of the gas forming on the plated surfaces exceeds the ambient pressure within the plating solution. Typically, applied pressure will slow the rate at which the gas may form and escape and consequently slow the rate at which the plating reaction will occur. Conversely, reduced pressure will speed the rate at which the gas can form and escape and consequently speed the rate at which the plating reaction will occur.

Assuming that control of the rate of plating is desired, the present invention permits such control by adjustment of pressure control valve 47. When speeding of the plating reaction is desired, pressure control valve 47 is manipulated to reduce the ambient pressure of the plating reaction within column A. As the pressure is reduced interior of column A, the gaseous by-products may readily escape thus speeding the plating reaction. Alternately, when slowing of the plating reaction is desired, pressure control valve 47 is manipulated to increase the ambient pressure of the plating reaction within column A. As the pressure is increased interior of column A, the gaseous by-products are retarded in their escape, thus slowing the plating reaction.

It may be desired to place more than one batch of particles F simultaneously within a column plating reactor. Such modifications will require more than one plating segments C.

With reference to FIG. 2, plating reactor A having multiple plating segments is illustrated. Reactor A comprises a glass cylinder 14, a bottom plate 15 and a top plate 16 which is substantially identical to the plating column A previously illustrated in FIG. 1. This column A differs only in the insertion of multiple vibrating screens E' and E''.

Regarding vibrating screens E' and E'', the screen mounting assembly 20 for each vibrating screen E' and E'' is constructed in an identical fashion to the vibrating screen of FIG. 1. Rod 30, however, transmits vibration to both vibrating screens E' and E''..

First plating segment C' is defined between first vibrating screen E' and second vibrating screen E''. Similarly, second plating segment C'' is defined between second vibrating screen E'' and lower stationary screen D. As is apparent, by the presence of additional vibrating screens E, column 14 may be provided with as many plating segments C as may be desired.

Although the foregoing invention has been described in some detail by way of illustration and example for purposes of clarity and understanding, it is to be understood that certain changes and modifications may be practiced within the spirit of the invention as limited only by the scope of the appended claims.

What is claimed is:
1. A plating process for uniformly plating particles of small dimension with metal, said process comprising: providing a bath of plating solution having metallic ions; submerging said particles interior of said bath; activating a first zone of said bath at a first elevation within said bath to provide a plating ambient wherein deposit of said metallic ions on said particles occurs; maintaining a second zone of said bath at a second elevation with an ambient whereby plating is retarded with said second zone placed so that one of said zones overlies the other of said zones; vertically flowing plating solution through said zones to maintain particles having insufficient plating deposit thereon in said first zone and particles having sufficient plating deposit thereon in said second zone.
2. A plating process according to claim 1 and having the additional step of: controlling the velocity of said vertical flowing of plating solution to control the amount of plating material deposited on said uniformly sized particles.
3. A plating process according to claim 1 and wherein said activating of said first zone comprises: maintaining an electric field in said first zone.
4. A plating process according to claim 1 and wherein said activating of said first zone comprises: maintaining a temperature within said first zone whereby plating is accelerated.

5. A plating process according to claim 1 having the additional step of: flushing said plating solution from said bath when said confined particles move from said first zone to said second zone within said plating segment.

References Cited

UNITED STATES PATENTS

521,991 6/1894 Sachs __________________ 204—10

1,789,443 1/1931 Levin ___________ 204—20
2,586,818 2/1952 Harms ___________ 117—100
2,683,686 7/1954 Matsukawa __________ 204—23
2,939,804 6/1960 Schossberger _________ 117—100

Ta-HSUNG TUNG, Primary Examiner
T. TUFARIELLO, Assistant Examiner

U.S. Cl. X.R.

117—100; 118—429; 204—23, 222, 273, 275