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Eisner

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[54] **BI-POLAR ACRIVATING PARTICLES FOR ELECTRODEPOSITION PROCESS**

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[73] Assignee: **Norton Company,** Troy, N.Y.

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Related U.S. Application Data

[62] Division of Ser. No. 147,409, May 27, 1971, Pat. No. 3,699,017.

[52] **U.S. Cl.**..... **117/212,** 117/230, 204/45 R, 204/49, 204/52 R, 204/DIG. 10, 204/279

[51] **Int. Cl.**..... **B44d 1/18,** B44d 1/34

[58] **Field of Search**..... 117/212, 100 M, 230, 201; 204/52 R, 45, 49, 279, 242, DIG. 10

[56] **References Cited**

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[57] **ABSTRACT**

An electrically-conductive mass in the form of a small particle encapsulated in a hard non-conductive outer sheath having at least one opening in such sheath permitting contact between such conductive mass and a liquid electrolyte when the particle is immersed in such electrolyte. Preferably, the conductive mass and/or the outer sheath is so formed or treated that the conductive mass does not protrude beyond the sheath at any of said openings.

4 Claims, 4 Drawing Figures

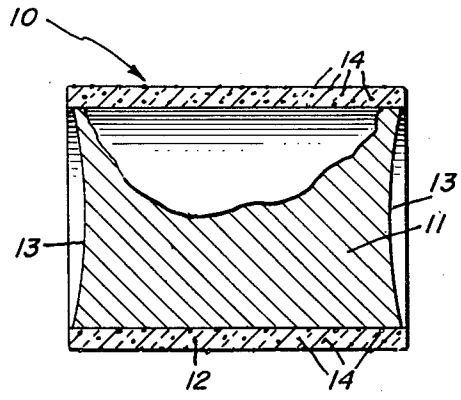


Fig. 1.

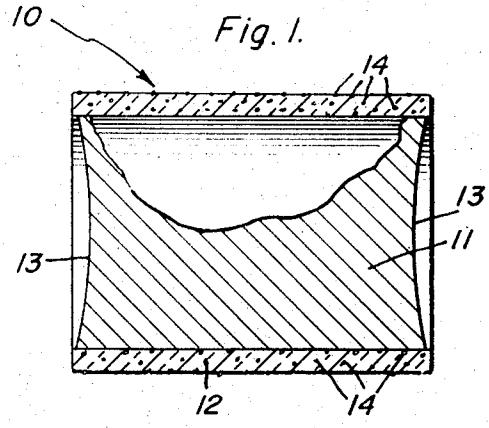


Fig. 2.

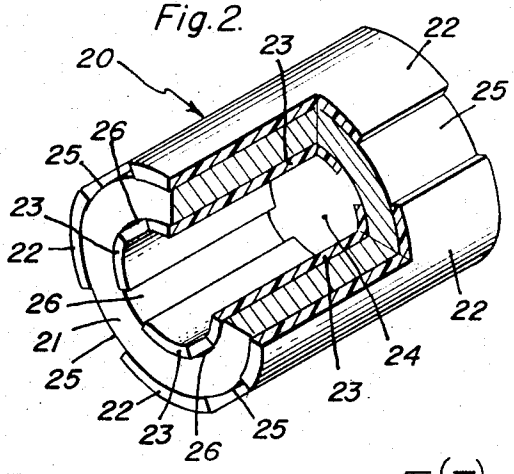


Fig. 3.

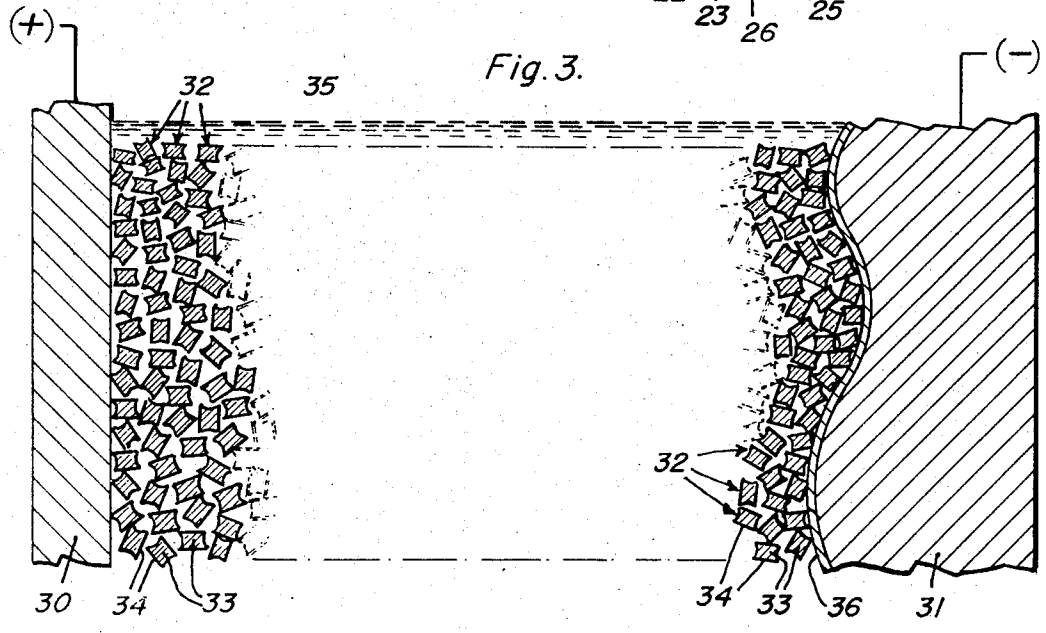
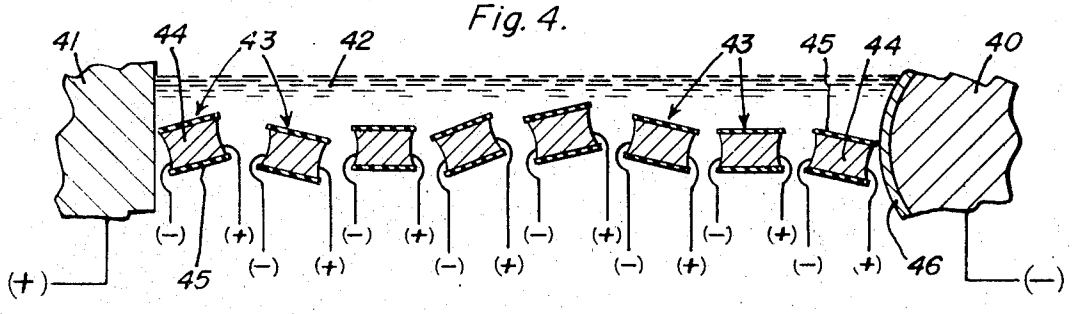


Fig. 4.



BI-POLAR ACRIVATING PARTICLES FOR ELECTRODEPOSITION PROCESS

This is a division, of application Ser. No. 147,409, filed May 27, 1971 now U.S. Pat. No. 3,699,017.

FIELD OF THE INVENTION

The prsent invention relates to electrodeposition of metal onto a substrate from a liquid electrolyte solution by imposed current flow. It is particularly adapted for use in a system such as those disclosed and claimed in the copending applications of Steve Eisner, Ser. No. 102,287, filed Dec. 29, 1970 now U.S. Pat. No. 3,699,014 and of Norvell E. Wisdom, Jr., Ser. No. 140,143, filed May 4, 1971 now U.S. Pat. No. 3,699,015, (which are more fully described below).

DESCRIPTION OF THE PRIOR ART

Particulate material of various kinds has heretofore been incorporated into plating baths, generally with the idea that it would polish or densify plate laid down by conventional means and at conventional rates. Generally, this material has been incorporated in the form of a suspension with agitation of the liquid electrolyte serving to keep this material suspended therein. In at least one instance, (U.S. Pat. No. 1,594,509), the particles were relatively large and motion of the container served to cause these materials to beat or pound the plate after it was deposited to densify the plate. In all of this type of art, an extremely low particle to liquid volume ratio was employed. More recently, French 1,500,269 recognized that incorporating a relatively high volume of particles to liquid in the form of a fluidized bed caused a reduction in cell voltage at constant relatively low current densities in a specialized plating system as compared with the voltage resulting from high flow rates of electrolyte only. This patent also suggests that conductive particles could be used if desired. Conductive particles have also been used to form fluidized bed electrodes in work sponsored by the National Research and Development Council in Great Britain. Still more recently, the aforementioned processes described and claimed in U.S. applications, Ser. Nos. 102,287 now U.S. Pat. No. 3,699,014 and 140,143 now U.S. Pat. No. 3,699,015 have recognized that going to very high particle to liquid ratios and utilizing externally applied vibratory forces to set and maintain small, hard particles in motion over the surfaces of the article being plated throughout the entire period of imposed current flow permitted some material improvements in plating rates in the case of Ser. No. 102,287 now U.S. Pat. No. 3,699,014 and in throwing power in the case of Ser. No. 140,143 now U.S. Pat. No. 3,699,015. The throwing power improvement of this latter case is achieved at the expense of improved speed of deposit although rates equivalent to or slightly greater than conventional can still be achieved. As is covered in detail in such application, the throwing power improvement is obtained by so arranging the system as to bring into the plating zone electrolyte essentially solely as a surface layer on each individual particle. The process of Ser. No. 102,287 now U.S. Pat. No. 3,699,014, on the other hand, has electrolyte present in all of the interstices between the activating particles in the plating zone as well as on the surfaces of such particles, and does achieve substantial increases in plating rates both over conventional processes and over the process of Ser. No. 140,143 now U.S. Pat. No. 3,699,015 as a result. The throwing power of the process of Ser. No. 102,287 now U.S. Pat. No. 3,699,014, however, is not much improved over that of conventional systems.

The processes of Ser. Nos. 102,287 now U.S. Pat. No. 3,699,014 and 140,143 now U.S. Pat. No. 3,699,015 in which the present invention is particularly applicable generally rely on "activating" the surface of an electrodeposit by repeated contacts over very short time intervals with a plurality of small "dynamically hard" particles. "Activating" the surface means so treating the surface as to create at such surface a high tendency to utilize the imposed current to deposit metal in sound, adherent form rather than as powder or dendrites. "Dynamically hard" is defined to mean that the particles act, through a combination of their actual hardness, mass, impact speed and pressure, in such a manner as to activate the electrodeposit surface and generally a criteria of this hardness is the formation in the surface of the deposit of visible scratch patterns (visible at least under a magnification of 10,000X or less). The particles are placed in a container capable of being vibrated by externally imposed forces which imparts both a macro- and a micro-motion to such particles as a result of impacts between such particles and the walls of the container. Electrolyte is placed in such container along with the particles with the electrolyte level being above or at least substantially filling the plating zone in the case of the process of Ser. No. 102,287 now U.S. Pat. No. 3,699,014 and below or just barely into such zone in the case of the process of Ser. No. 140,143 now U.S. Pat. No. 3,699,015. Motion is initiated in each instance before any current flow is imposed and such motion is continued throughout the plating cycle. Generally, the cathodic part being plated is fixtured in the container although it can be arranged so as to move therethrough in a predetermined and fixed path. In both of these processes, the particles are entirely or at least predominately non-conductive electrically. It is possible, as disclosed in these aforementioned applications, to use a small amount, i.e., up to about 5 percent by volume of conductive particles along with the major portion of non-conductive particles. The present invention is directed to a type of conductive particle which can be used as the sole particle type in processes such as those described above.

SUMMARY

The present invention involves the discovery that two problems involved in the activating particle-vibratory container processes discussed above can be solved by the use of a particular type of activating particle. First, in such a process, the extremely high volume of particles to electrolyte tends to create a serious interference with current flow between the anodes and the cathode — the particles serving to cause a plurality of tortuous, interrupted paths for such current to follow. Secondly, whereas the volume of electrolyte in one instance is sufficiently high to permit rapid deposition rates, throwing power is not improved. In the other instances where throwing power is improved, the electrolyte volume is so low as to limit the speed to essentially conventional rates. It would be desirable to increase the throwing power without this decrease in plating rate.

By using as the activating particles a composite particle having a body or core portion formed of electrically conductive material (usually but not necessarily the same metal as is intended to be deposited) with a pro-

tective outer covering or sheath or non-conductive material which is sufficiently hard as to permit the particle to act "dynamically hard," (generally such sheath must have a Knoop hardness of about 500 or greater) where such outer sheath is perforated or open at least at one point on the surface of the particle to expose the metal or electrically-conductive underlying core portion, both of the above problems can be solved. The particle cores, being electrically conductive, provide reasonably direct paths for current flow and the particles themselves act as bi-polar electrodes — the side of the exposed metal toward the anode at any given instant tending to act as a cathode and having metal deposited on the core with the side towards the cathode tending to act as an anode and giving up metal ions. With the high particle density, those particles immediately adjacent the surface being plated provide a high supply of metal ions at the point necessary to afford an adequate supply for even, uniform thickness deposition even on a contoured surface.

DRAWINGS

FIG. 1 is a view in cross section of a typical particle of the present invention.

FIG. 2 is a perspective view in partial cross section of a variation in shape of a particle of the present invention.

FIG. 3 is a schematic illustration showing the relationship of particles of the present invention to an anode and cathode.

FIG. 4 is an idealized view schematically illustrating one current path through the system shown in FIG. 3 and illustrating the bi-polar effect.

DESCRIPTION OF PREFERRED EMBODIMENTS

The activating particles of the present invention are preferably formed with a metallic core of the metal to be deposited in the system in which the particles are to be used, i.e., for a copper plating system, the particle core is copper and for a nickel plating system, the core is nickel. The surrounding non-conductive sheath should preferably be of a relatively hard, impact-transmitting material, i.e., having relatively high non-energy-absorbing characteristics. Most of the thermosetting resins fall into this category as do the ceramic bonds used in and known to the art of bonded abrasives. In addition to being non-energy-absorbing and non-conductive, the sheath should possess the property of being easily wet by the electrolyte in which it is to be used and should also be resistant to chemical attack by such electrolyte. The hardness of the outer sheath should generally be at least slightly harder than that of the metal to be plated but since higher hardnesses do not appear to produce adverse effects, it is preferred, in order to avoid experimentation to utilize for such sheaths materials having a hardness of about Knoop 500 or greater. For the process of Ser. No. 102,287 now U.S. Pat. No. 3,699,014, smooth surfaced particles are satisfactory although particles with rough surfaces are satisfactory. However, in the process of Ser. No. 140,143 now U.S. Pat. No. 3,699,015, where the electrolyte in the plating zone (once movement of the particles is initiated) is carried into such zone on the surface of the particles, a micro-roughness is an essential feature of the particle surface.

Suitable materials for forming the particles of the present invention include, as indicated above, any conductive material which will accept a metal deposit thereon and preferably the specific metal which the particle is to be used to help deposit. These include all of the conductive metals which are capable of electrodeposition. As to the sheath, the preferred coating is a ceramic such as aluminum oxide, silicon carbide, boron carbide or the like, and again, preferably, such coating will have embedded therein or anchored thereby a plurality of very small particles of any of the conventionally-used abrasive materials such as silicon carbide, aluminum oxide, flint, emery, garnet or the like. These very small particles in the sheath will generally have an average diameter in the vicinity of 1 to 10 microns. Also, thermosetting resins, resistant to the electrolyte with which the particles are to be used, may also be used to form the sheath either alone or again with the occulsion of small abrasive particles. Examples of such resins include phenolics, polyesters, urea-formaldehyde resins, polyethers, polyamides or the like.

The size of the particles in the present invention should generally be in the range of 0.01 to 0.25 inches in average maximum dimension with the preferred range being between 0.02 and 0.125 inches. Particles of varying sizes and shapes may be blended together to vary the degree of activation of the electrodeposit if desired.

The shape of the particles may vary within wide limits from extremely irregular to very uniform geometric shapes. Preferably, for ease in formation, the particles are in the shape of short cylinders although as is illustrated in FIG. 2, more complex shapes are contemplated and may be particularly desirable in some instances.

Referring now to the drawings, FIG. 1 illustrates in cross section a preferred form of the particles of the present invention. The particle **10** consists of an electrically-conductive metal core portion **11** and a non-conductive sheath portion **12** surrounding the core portion **11** except at the ends **13**. Embedded in the sheath portion **12** are a plurality of small hard particles **14**. The ends **13** of core portion **11** are dished-in so that the metal **11** does not extend out as far as the protecting non-conductive sheath portion **12**. This is accomplished as is described below by etching the particles after they are formed. As illustrated, the non-conductive sheath **12** is a ceramic coating containing small abrasive grains. The particle is formed by coating a continuous small-diameter metal wire or rod with a ceramic mixture, fusing the ceramic to cause it to harden and become permanently bonded to the wire, and then severing the coated wire at short intervals to produce short coated cylinders open at each end. The particles are then immersed in an etching solution, e.g. nitric acid for copper core particles, and left for approximately 1 to 2 seconds with mild agitation to cause the exposed wire cores to be etched or eaten away. This produces a particle with the metal core inset as shown at **13** in FIG. 1 whereby direct electrical contact from one particle to another is minimized or prevented. This prevents any shorting across the particle path from anode to cathode in the plating system.

FIG. 2 illustrates a modified version of the invention wherein the particle **20** is a doughnut shape. Again, a metal or conductive core **21** is partially encased in a sheath **22**. Here the sheath **22** is illustrated as a hard resin coating which provides incremental covering sec-

tions **22** around the outer periphery of the core **21** and additional covering sections **23,** not necessarily corresponding to **22,** around the inner periphery of core **21.** As shown, the sheathed core particle **20** has an open central portion **24** which provides more room for electrolyte movement and additionally increases the surface area of the particle **20** exposed to such electrolyte over that available with a solid particle of the same external dimensions. Portions of the core **21** are exposed between the outer sheath segments **22** as shown at **25** and between the inner sheath segments **23** as shown at **26.**

In operation, these particles, in accordance with the processes described in the aforementioned copending applications, are literally packed in very close relationship to one another in the plating system — substantially completely filling the space between the anode and cathode as is illustrated in FIG. **3** (as indicated in the said copending applications, the difference between the number of particles in the plating zone with the system at rest and with vibration imposed on the system is not greater than 5 percent). FIG. **3** schematically shows a portion of a plating sytem having a non-conforming anode **30** and a contoured cathode **31.** Interposed between anode **30** and cathode **31** is a plurality of varying sized particles **32** shown here in cross section to illustrate the conductive core **33** and protective non-conductive sheath **34.** Although the electrolyte is interspersed throughout the interstices between particles **32,** it is difficult to illustrate and hence is indicated only at **35** (above the illustration of the particles **32**) with the understanding that actually the particles **32** completely cover the entire cathode surface during plating and are either interspered with the electrolyte **35** or carry the same on their outer surfaces. It will be noted that no particular orientation of these particles can be observed and actually they tend to both rotate in their micro-orbits and move relative to the anode and cathode in their macro-orbit throughout the plating cycle so that their orientation to one another and to the fixed anode and cathode is constantly changing under the imposed external vibration. As shown in FIG. **3,** an electrodeposit **36** is forming on cathode **31** and, because of the bi-polar effect of these particles, such deposit **36** is relatively uniform in thickness despite the varying contours of cathode **31** upon which it is being deposited.

FIG. **4** schematically illustrates the function of the particle structure of the present invention. Again a cathode **40** and anode **41** is provided in an electrolyte **42.** An idealized single chain of particles **43** is shown to permit clear illustration. Each particle **43,** as shown, has the recessed conductive core portion **44** and the surrounding non-conductive sheath **45.** It is clear that current flow between the cathode **40** and anode **41** will take place from the electrode to the electrolyte, through the conductive core of a particle to the electrolyte, through the next particle core, etc., until the other electrode is reached. If these were all non-conductive particles, the current flow would obviously have to be through the electrolyte only and the path of such flow would be much more indirect with consequent loss of efficiency and increase in the IR heating of the electrolyte. Also shown in this diagrammatic illustration is the bi-polar effect. At any given instant the particles will have a fixed orientation to one another and to the electrodes. What is shown here is a look at this particular chain of particles as they might appear at a given instant. The exposed core portion **44** of each particle will act as an electrode. That portion of the core of the particle closest to anode **41** will act as a cathode and metal will deposit out thereon in such instant. Likewise, the opposite end of such core will become anodic and will tend to give off metal ions to the surrounding electrolyte. This is continued across the chain as illustrated by the bracketed positive and negative signs until the surface of the electrodeposit **46** is reached. At that point, the core portion **44** of the particle **43** closest to the cathodic electrodeposit surface **46** will act anodically and will tend to give off metal ions extremely close to the electrodeposit surface. This ready supply of metal ions in close proximity to the surface activated by the impact of the particles **43** causes the plate to build up uniformly despite the varying contours of the surface of the cathode **40.**

EXAMPLE 1

Using a 1/64 inch diameter copper wire as the core-forming member, particles according to the present invention can be prepared by suspending 12 inch long sections of such wire inside 1/32 inch diameter holes in a graphite block. The lower portion of the block is then immersed in a bath of molten alumina. A vacuum is then pulled on the holes and the molten alumina flows up and around the wire sections inside the graphite block. The block is then broken into sections between the wire segments and is burned to remove the coated wire segments. Using diamond saws, the ceramic coated wire is then cut into 1/32 inch long pieces which may be used as is for the purposes of the present invention or preferably after a short etching with concentrated nitric acid to insure that the metal core is recessed inside the ceramic sheath. If desired, the small pieces may be pre-tumbled before using in one of the described electrodeposition processes in order to roughen the surface of the alumina.

EXAMPLE 2

Another manner in which particles of the present invention may be prepared is exemplified by the preparation of a slurry of fine abrasive grain (Grit 1,000 Silicon Carbide) in a thermosetting phenolic resin binder. Such slurry preparations are well known in the abrasive art and the viscosity will be adjusted as desired to provide for spray or dip application. Preferably, the wire to be coated (1/64 inch nickel wire) is passed in continuous form through a bath of this slurry and slowly rotated in a forced hot air draft for about one hour to permit the resin to set up slightly. The wire is then passed into an oven heated to about 300°F. for 2½–3 hours to cause the resin coating to cure. After curing to a hard state, the coated wire is cut into short (1/32 inch) segments by diamond saws, etched by a 1–3 second immersion in concentrated nitric acid, given a thorough water wash and then is ready for use in an electrodeposition process.

EXAMPLE 3

3,500 cc of the bi-polar activating particles of Example 1 (etched to recess the metal core portions) were combined with 6,000 cc of copper sulfate plating solution (300 grams/liter $CuSO_4.5H_2O$ and 100 grams/liter H_2SO_4 containing 0.5 percent by volume of UBAC No. 1—a commercially available brightener

for copper). The mixture was then placed in a ⅓ cubic foot capacity vibratory finishing machine (Elliot Vibratub). The cathode was a steel doorknob to which a copper strike had first been applied. The doorknob was mounted in a vertical position with the knob end upwards and surrounded by four equally-spaced ½ inch square copper bars which acted as anodes. The bars formed a hollow square with the doorknob in the center with approximately 1 inch distance between the cathode and each anode bar. Plating was carried out with the Vibratub operating at 2,100 cycles per minute with a tub amplitude of ⅛ inch. A current of 50 amps was applied which calculated out to a current density of approximately 750 amps/ft.^{2} at the cathode. Plating was carried out for 2 minutes at the end of which a smooth, uniform copper plate of 1.2 ± 0.1 mils was obtained over the entire doorknob. Plating an identical doorknob under the same conditions but utilized as the activating particles non-conductive Grit 30 sintered bauxite particles gave a plate of similar appearance but one which varied in thickness from 0.7 mils on the shank to 2.4 mils on the outer curve of the head portion.

In addition to forming the particles as illustrated in Examples 1 and 2 above, ceramic coatings can be applied by co-extrusion of the metal core with a ceramic mix or by swagging or rolling the wire in a fine grain ceramic mix followed by encasing the coated wire in a metal sheath which is dissolved or cut away after sintering the ceramic. Also, in the case of resin coatings, the slurry can be sprayed onto the wire or applied by coating rolls if desired. Cylindrical particles can be obtained by rolling metal balls in a slurry and after the resin mixture has set up, abrading away the resin sheath on one surface of the balls.

I claim:

1. A bi-polar conductive particle for use in electrochemical processes which comprises:

a. a conductive metal core member; and

b. a hard, non-conductive sheath completely encapsulating said core member except at diametrically opposed openings therein which permit contact between such conductive core and a liquid electrolyte when the particle is immersed in such electrolyte;

c. said core member being recessed at said openings in said non-conductive sheath.

2. A particle as in claim **1** wherein said non-conductive sheath is formed from a ceramic material.

3. A particle as in claim **1** wherein said non-conductive sheath is formed from a thermosetting resin.

4. A particle as in claim **1** wherein a plurality of small, hard, non-conductive particles are embedded in the material forming said non-conductive sheath.

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