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Christini et al.

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[54] **ELECTROLESS PLATING APPARATUS**

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[52] **U.S. Cl.** **118/417,** 118/429

[51] **Int. Cl.** **B05c 3/04**

[58] **Field of Search** .... 118/19, 423, 425, 429, 118/417, 29, 30; 134/191; 117/113, 114, 116, 117, 100 A, 100 L, 109; 204/273, 275; 259/95; 156/345

[56] **References Cited**

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Primary Examiner—Morris Kaplan

[57] **ABSTRACT**

Method and apparatus for concomitant particulate deposition in electroless plating, and the product thereof, wherein objects to be plated are subjected to tumbling during the plating process.

2 Claims, 7 Drawing Figures

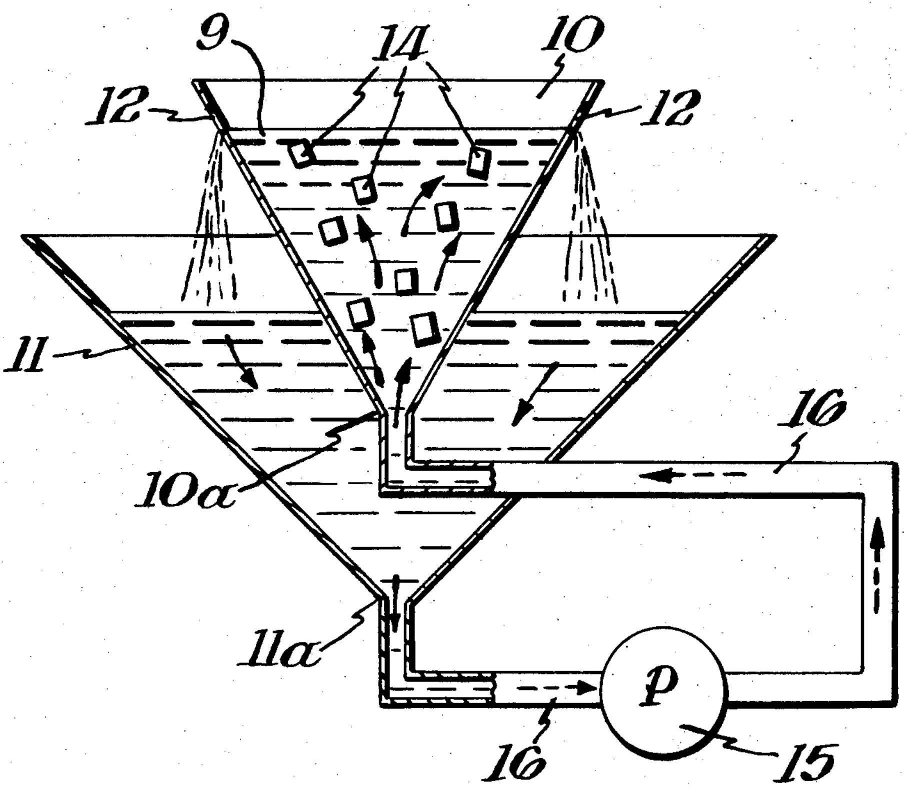

Fig.1.

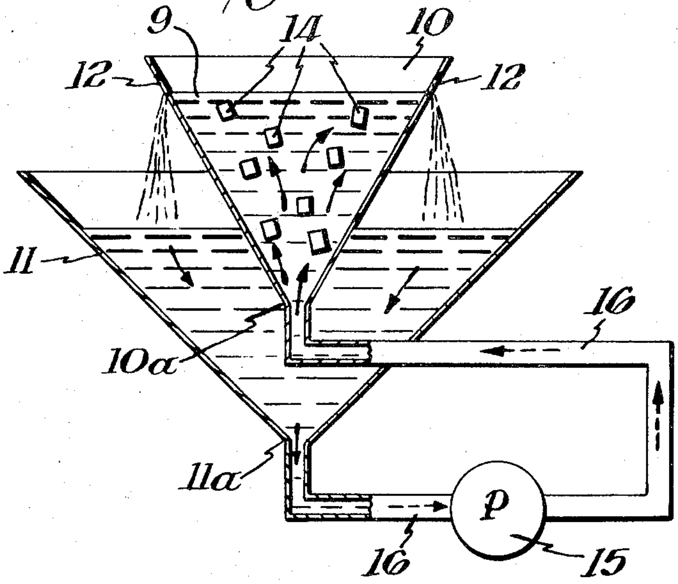

Fig.2.

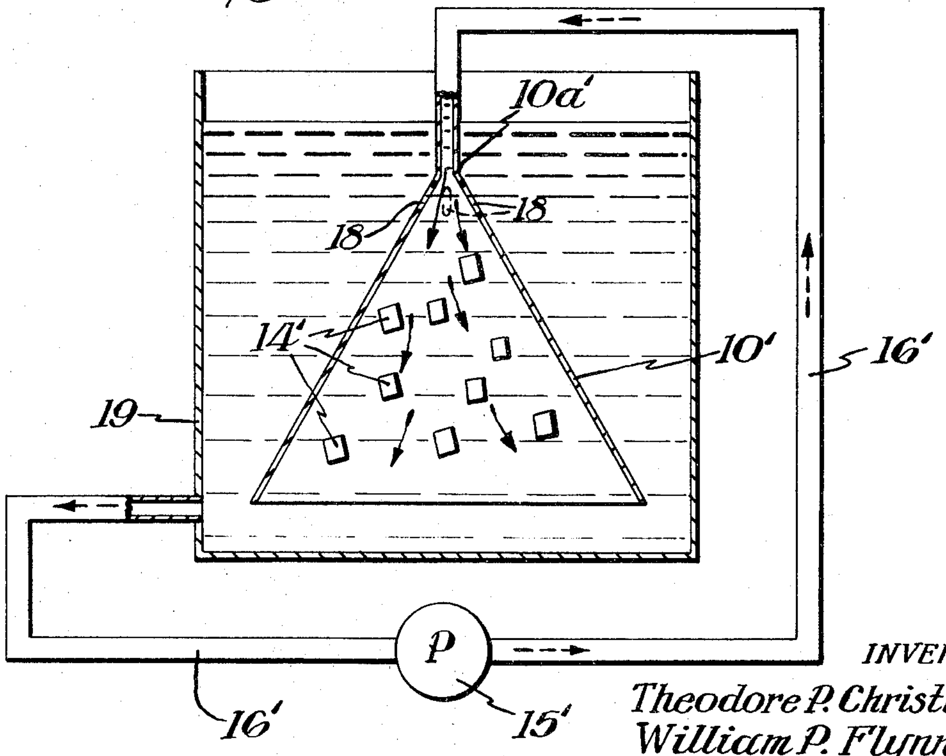

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Fig. 3A.

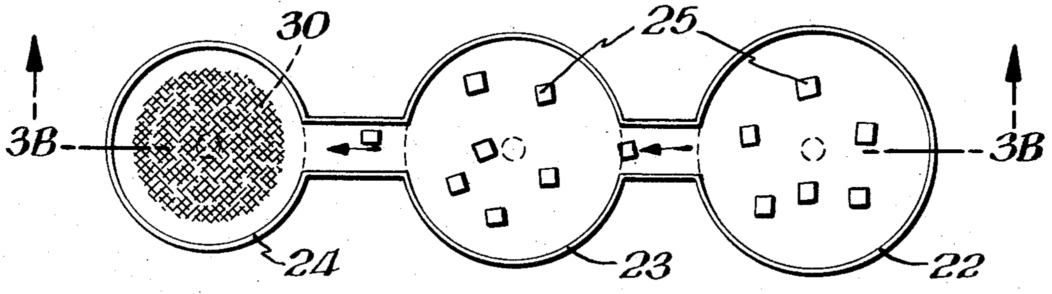
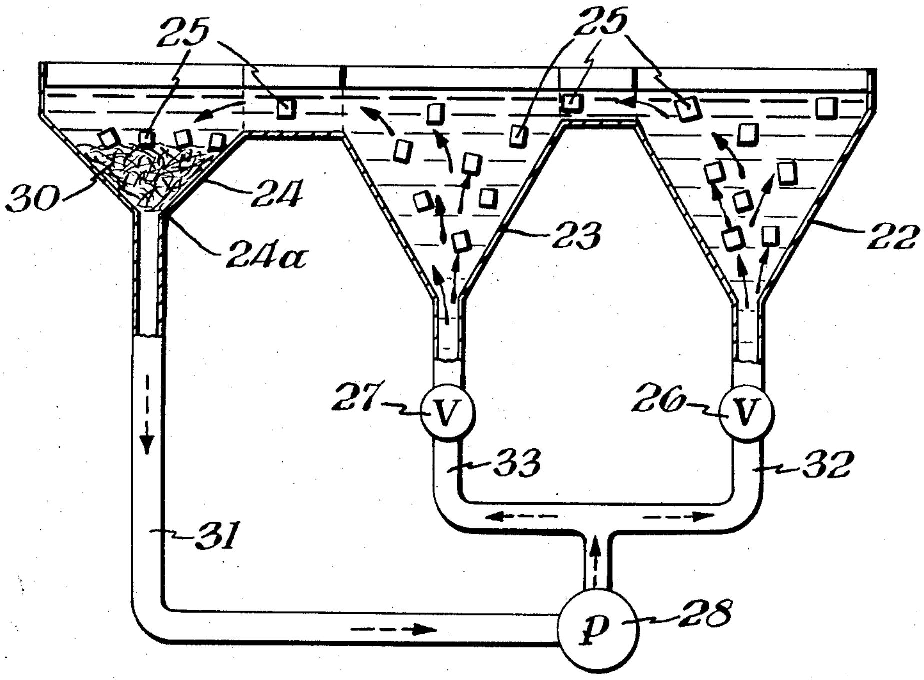


Fig. 3B.



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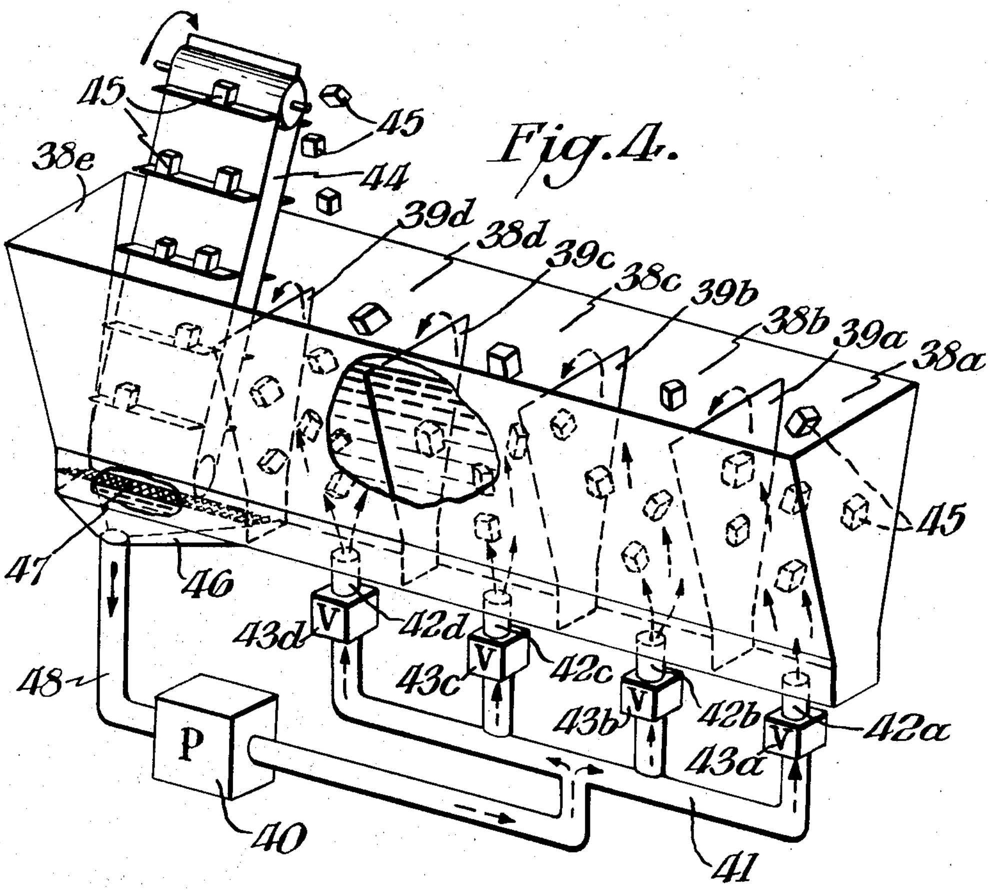

Fig. 4.

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Fig. 5A.

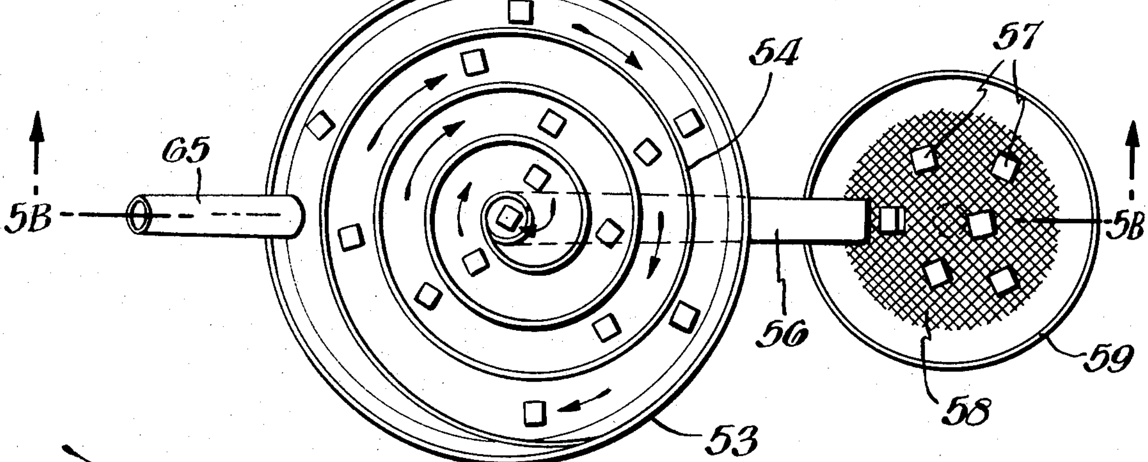
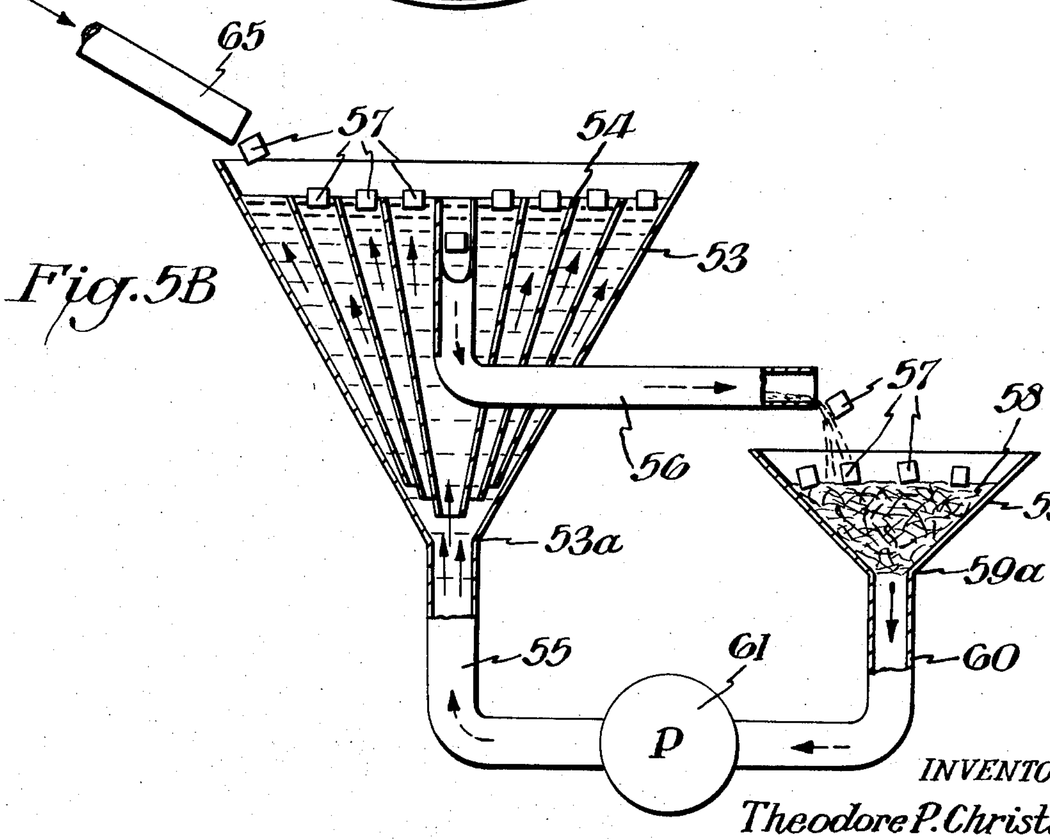


Fig. 5B



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ELECTROLESS PLATING APPARATUS

BRIEF SUMMARY OF THE INVENTION

Generally, this invention comprises apparatus for concomitant particulate deposition in electroless plating comprising contacting articles to be plated with a continuously circulating electroless plating solution containing suspended particulate material which it is desired to deposit on said articles, and subjecting the articles to tumbling within the plating solution for a sufficient time to obtain a preselected amount of electroless plating with concomitant deposition of particulate material on the articles, and the product thereof.

DRAWINGS

The following schematic drawings depict preferred embodiments of apparatus for carrying out the invention, in which:

FIG. **1** is a cross-sectional side elevation view of an apparatus wherein the plating solution is supplied in generally upward vertical flow,

FIG. **2** is a cross-sectional side elevation view of an apparatus for plating buoyant articles wherein the plating solution is supplied in generally downward vertical flow,

FIGS. **3A** and **3B** are, respectively, plan and side elevation cross-sectional views of a first design of apparatus for conducting plating in sequential stages,

FIG. **4** is a partially cross-sectional perspective view of a second design of apparatus for conducting plating in sequential stages, and

FIGS. **5A** and **5B** are, respectively, plan and side elevation cross-sectional views of an apparatus incorporating a continuous spiral baffle for effecting continuous, as distinguished from batch, plating.

PRESENT PRACTICE

Electroless metal plating of both electrically conductive and electrically non-conductive articles is known to the prior art; however, there exist serious problems as regards plating bath stability.

Thus, in a typical situation, described in U.S. Pat. No. 3,234,031, involving nickel plating as an example, the soluble nickel salt, in this instance dissolved $NiCl_2 \cdot 6H_2O$, is reduced by an alkali metal borohydride ($NaBH_4$) in order to plate out nickel on an object immersed in the bath. The Patent reported prior art difficulties with more or less sudden bath decomposition, during which Ni metal flakes either formed, or a heavy black precipitate dropped out when the concentration of the plating metal in the baths had decreased from 10 to 25 percent in the course of plating. The Patent solution to this problem was to add an organic divalent sulfur compound as stabilizer.

Also, U.S. Pat. No. 2,847,327 reported similar bath instability, which was reportedly cured by adding critical amounts of long chain aliphatic organic compounds.

Finally, U.S. Pat. No. 3,261,711 offered the solution of bubbling oxygen continuously through the bath to maintain the oxygen content at the saturated level.

None of these Patents was concerned with the concomitant deposition of suspended particulate material during the plating, and they are mentioned here only because they point up a serious problem of plating bath instability, even in the absence of suspended particulate substances.

THE INVENTION

This invention constitutes an apparatus for surface coating either electrically conductive or non-conductive articles, which can typically be metallic, polymeric, ceramic or even wooden objects, by electroless plating deposition of metal which concomitantly carries with it a particulate substance suspended in the plating bath, together with the product obtained. The coatings obtained comprise a metallic-alloy matrix within which is uniformly distributed the particulate substance as dispersed phase.

As an example, there is hereinafter described (Example 4) the deposition of a wear-resisting coating on a polymeric base, specifically a twisting jet utilized in the manufacture of synthetic textile yarns, wherein the objects coated have slots as narrow as 10 mils wide and bores as small as 10 mils diameter, so that the problems of smooth uniform coating are formidable indeed, due to requirements of fine dimensional control maintainence. However, the invention is not, of course, limited to these items and is broadly applicable wherever a continuous metal coating incorporating distributed particulate material is the objective. Thus, caralyst preparation, super-conductor manufacture and many other utilizations are practicable.

Conventional electroplating processes have been hitherto utilized to effect simultaneous electrodeposition of metals and hard particles as additives, in order to provide enhanced wear resistance. However, these have not been entirely satisfactory, especially when the items to be coated have recesses or hollow interiors, because the throwing power is inadequate to give uniform coverage. This is particularly the case for yarn guides and yarn-treating jets, which require high uniformity in coating composition in all regions contacted by a moving yarn line.

Moreover, high coating adherence is an absolute requirement, and the coatings of this invention are extremely adherent, so that there is no requirement for additional bonding steps, such as pressure sintering, or the like.

The feasibility of fine-particle incorporations in electroless baths during plating has been doubted until now, because of the strong tendency towards spontaneous bath decomposition whenever suspensoids of any kind exist which can serve as nuclei for the random decomposition of the bath and the heavy drop out of black precipitate, hereinbefore reported in the prior art. Such precipitation brings further plating to an immediate halt or, alternatively, produces rough, unsightly deposits which are completely unacceptable.

Applicants have found, surprisingly, that by continuously circulating their plating baths in the course of plating and, at the same time tumbling their articles to be plated within the bath, they not only obtain complete bath stability but, equally as important, obtain greatly improved plate coatings within which the particulate additive distribution is extremely uniform.

Bath compositions suitable for use in this invention can cover a wide range; however, those operating at lower temperatures, e.g., in the range from about 30°C. to 60°C. are particularly preferred. The best available baths from the standpoint of inherent stability are, of course, preferred, and those of U.S. Pat. No. 3,234,031 utilizing amine boranes as reductants have worked well.

Typical metallic-alloy matrices deposited can consist of the Ni-P alloy coatings deposited by the processes taught in U.S. Pat. Nos. 2,532,283; 2,658,841; 2,658,842, and others. Or one can equally well utilize the Ni-B alloy coatings of U.S. Pat. Nos. 3,096,182; 3,062,666; 3,338,729; and 3,234,031.

Electroless plating, which is sometimes referred to as chemical reduction plating, occurs by catalytic reaction between metal ions or compounds and a reducing agent dissolved in an appropriate solvent. Thus, the electroless Ni-P coating processes hereinabove mentioned typically proceed when aqueous solutions containing the reductant $H_2PO_2^-$ ions exist within a bath containing nickel ions supplied by dissolved nickel salts. Similarly, the electroless Ni-B coating processes typically proceed when aqueous solutions containing a boron reducing agent, such as BH_4^- ions or dimethylamine borane, are present in the nickel ion bath. All practical electroless plating baths also contain buffers, e.g., salts of weak carboxylic or dibasic acids, to prevent rapid changes of pH, plus at least one of a large variety of chemical additives which have been found to stabilize against spontaneous bath decomposition.

Electroless plating is an autocatalytic process in the sense that the coating deposited serves as a catalyst for continuation of the plating action. Once plating has been initiated on the surface of a metallic, ceramic, or polymeric substrate, it continues as long as the substrate remains in contact with the plating solution. Because a uniform coating of any desired thickness can be applied by direct chemical reaction, without the passage of an electric current, the process was denoted "electroless plating" by Brenner and Riddell, who developed the first practical Ni-P processes (refer to J. Research, National Bureau of Standards, Vol. 37, p. 31 (1946), Brenner, A. and Riddell, G. E.).

The phase dispersed in the metallic alloy coatings of this invention can consist of a broad variety of particulate materials. Where wear resistance is the desideratum, hard inorganic particles such as oxides, carbides, nitrides, silicides, borides, diamond metallic or various intermetallic compounds are suitable.

The particles are preferably approximately equiaxial in shape, with an average size ranging from about 0.1μ to about 20μ, and a length-to-width ratio ranging from about 2:1 to about 20:1. Typical powders are described in the following:

TABLE I

Chemical Formula	Crystal Structure	Morphology		Comments
		Shape	Average Size, μ	
αAl_2O_3 (Linde A)	hexagonal	equiaxed	0.3	levigated, uniform size
αAl_2O_3 (Alundum)	hexagonal	acicular	l = 20; w = 10	–600 mesh
γAl_2O_3	cubic	equiaxed	0.1	levigated, uniform size
TiO_2	tetragonal	acicular	l = 3 ; w = 0.2	

Broadly, the process of this invention is concerned with the handling of particle additives in the range of about $0.05\mu - 100\mu$ particle size while controlling the bath agitation to maintain these particles in suspension for a time sufficient to effect composite plating of an immersed substrate, during which time bath conditions are maintained to achieve optimum stability and service life.

Particle settling rate is a function of particle size as well as the viscosity of the plating bath. Settling is also affected by particle concentrations, or loading, and degree of bath agitation. Plating rate, on the other hand, is influenced by many factors, which include among others (a) pH of the plating solution, (b) concentration of the reductant, (c) temperature of plating bath, (d) concentration of metal ions, and (e) ratio of bath volume to plating area.

Some plating of the metal onto the fine particles while they are in suspension can occur, depending upon the nature of the particles and whether they have been made catalytically active. Ordinarily, no preparatory treatment of the fine particles is necessary. The surface of the object to be plated will, in general, have been prepared to receive an adherent coating of metal and occluded particles by a suitable cleaning and chemical pretreatment prior to the electroless plating procedure. In all cases, for nonconductive substrates, the article to be plated will have been given a preliminary metal "strike" to help secure the particles. The additions of particles to be occluded in the metal matrix can be kept in suspension for the required time periods by agitating the bath solution, which also causes the particles to be moved into contact with the surface to be plated.

The nature of bath agitation can have an important effect on the coatings obtained, predominant orientations of the particles sometimes resulting as a function of bath motion. In prior art apparatus, it has been observed that there can be preferential particle settling on horizontal surfaces, depending, in part, on particle size.

With this invention, it is practicable to preselect the concentration of additive particles in the composite coating to suit the article end use. Thus, coatings containing as little as 3 percent by volume of additive particles have been produced, whereas heavier contents of up to 15 percent by volume and greater were equally attainable.

The bath agitation resorted to in our process utilizes continuous circulation of the plating bath through a contacting zone of progressively expanding cross-section in order to obtain a tumbling suspension of the articles to be plated at all times during which they are in the plating zone.

Previously, it has been the practice to use plating racks for the suspension within the bath of articles to be plated. However, these racks are objectionable, in that there occurs wasteful plate deposition thereon, which often requires "stripping" after each plating cycle. In addition, racks have not provided adequate support for parts having a small-diameter, deep holes within which uniform penetration and distribution of the plating bath solution is required. Also, racks prevent complete encapsulation of articles to be plated, since there must be some point of attachment to, or bearing support provided by, the racks. Thus, the elimination of racks altogether, as has been done in our invention, is advantageous for numerous reasons.

In addition, the mode of agitation of this invention has increased the tolerance of electroless plating baths for particulate solids, so that very high levels, e.g., up to 15 g./l., have been utilized without inducing bath decomposition. This is an unexpected benefit, especially in electroless plating, which permits lay-down of very concentrated particulate inclusions. Moreover, effective particulate suspensions have been maintained over very long time periods, bath lives in excess of 60 hours being routinely obtained using our process.

In tumble plating with the apparatus hereinafter described, small plastic, ceramic or metal parts are conveniently handled in groups ranging from 1 to 100 in number.

The polymers employed were two varieties of commercially available plating grade acrylonitrile-butadiene-styrene, specifically, Borg Warner Co. EP3510 and the glass-fortified AF–1004 of Liquid Nitrogen Processing Corporation.

The pretreatment was in the following sequence with a given group of articles placed in a stainless steel wire basket for convenient step-by-step handling:

1. Cleaning consisted of immersion in a proprietary alkaline cleaner (Marbon C–15) for 5 mins. at 65°C., in order to remove any grease or oil picked up in molding or handling operations.

2. The articles were then rinsed in hot and cold water for periods of 30 secs. each.

3. To promote coating adhesion to the article surfaces, the articles were chemically roughened by immersion in a proprietary chromic-sulfuric acid etch (e.g., Marbon E–20), immersion being for 4–6 mins. at 65°C. with mild agitation.

4. To remove any etch solution carry-over from step (3) the articles were rinsed in hot and cold water for 3 secs. each, followed by an ultrasonic water rinse of 2 mins. and a final rinse with running de-ionized water.

5. The articles were then sensitized by immersion in a proprietary (Enthone –432) bath which contains tin ions, the treatment being for 1½ mins. at room temperature, with the parts agitated in the bath.

6. Two de-ionized water rinses of 30 secs. duration under gentle agitation were next used to remove excess tin ions from the articles.

7. The articles were then placed in a proprietary activation bath (Enthone –440) containing Pd ions. The tin ions are thus further oxidized, under gentle agitation for 1.5 mins., thereupon reducing the Pd ions to metallic state.

8. The articles were then given two separate de-ionized water rinses of 30 secs. duration each, under gentle agitation.

9. Finally, the articles were placed in a Ni–B strike bath for 8–10 mins., the composition of this bath being identical with that of the particulate substance tumble plating bath hereinafter described, except free of particles for this pretreatment.

For ceramic parts, the preplate treatment is the same as hereinbefore described, except that a different treatment would be substituted for steps (2)–(4), inclusive, to achieve roughening of the ceramic surface. Thus, mechanical roughening might be substituted for chemical roughening.

For metal parts, yet another preplate treatment is required. Thus, a low C steel is prepared for plating by solvent degreasing (e.g., acetone or trichloroethylene), alkaline cleaner and then a rinse in 50 vol. percent HCl solution with rinses in de-ionized water after each step. The parts could then be placed directly in the tumble plating bath.

Referring now to FIG. **1,** a preferred design of tbmble plater according to this invention utilizes a large frustoconical funnel **10** coaxially disposed within, and somewhat above, a larger funnel **11** constituting a sump for reception of the gravity exhaust of plating solution **9** from funnel **10.** Peripherally spaced small size ports **12** in funnel **10** permit free overflow of solution (and suspended particulate solids) from this funnel without escape of the articles **14** being plated.

The plating solution is continuously recycled from the apex **11*a*** of the lower funnel via pump **15** and recirculating line **16,** which latter discharges into the apex **10*a*** of funnel **10.** A typical plating bath composition can be as taught in U.S. Pat. No. 3,234,031 supra, with bath temperatue maintained at about 55°C.

Periodic analyses of the bath ingredients are made, with replenishments as required.

Pretreated articles to be plated are dumped into funnel **10** and initially tend to settle to the bottom under gravitational force. However, as they approach the bottom they encounter the upwardly directed jet stream of suspended particles recycled by pump **15** via line **16.** A very complex article tumbling action results from the turbulence of the jet flow, the gradual deceleration of upward solution travel with progressive cross-sectional increase of funnel **10** and random collisions between the articles being plated. Most of these collisions tend to rotate the articles, causing a random non-directional agitation of the parts. The degree of bath agitation depends on the velocity of plating solution supply and the number of articles charged into the plater, as well as the size and degree of loading of suspended particles.

The advantage of a funnel **11** sump over a cylindrical reception vessel, for example, is that suspended solids are afforded no surfaces upon which they can deposit, so that uniform suspension concentrations are preserved indefinitely, In addition, the range of loading factor in terms of ratio of weight of powder to volume of solution is considerably broadened.

Prior practice has hitherto favored the use of more or less quiescent baths, free of turbulence. However, we have found that tumble plating is positively advantageous, because it favors the formation of uniform surface topography free from burrs and massive nodules. Moreover, there is obtained a more uniform dispersion of occluded particles in the plate coat. Elimination of article-holding racks permits easy inspection of individual articles in process by simply scooping them out as desired.

An extremely important advantage of tumble plating is the increased throwing power thereby obtained. This results from the impingement of a high-velocity stream of plating solution, containing suspended particles, which impacts all surfaces of the substrate plated in random manner within the bath. This unique action distinguishes tumble plating from conventional prior art barrel plating methods used in electroplating composites, affording the following advantages:

1. A high volume percentage of particles is incorporated into the plate coat at relatively low bath loading factors of weight of powder/liter plating solution.
2. Incorporation of particles over the entire surface, and into small diameter holes and narrow slots occurs
3. Greater breadth is achieved as regards the size and shape of particles which can be incorporated in composite coatings.

For example, our tests have shown that a composite electroless Ni–B coating with 13.1 percent of αAl_2O_3 can be deposited from a plating bath containing 15 g./l. of Linde A alumina powder. Electrodeposition of a nickel composite coating with a comparable volume percent requires a bath loading factor of the order of 50 to 150 g./l.

Articles having a wide range of densities and geometries can be plated by the method of this invention. Thus, for buoyant articles **14'**, the apparatus of FIG. **2** can be employed, which utilizes an inverted frustoconical funnel **10'** provided with ports **18** at its upper, constricted end through which the articles can be conveniently introduced. With this design a cylindrical sump **19** is provided in open communication at its lower end with funnel **10'**, recirculation of plating solution being obtained by pump **15'** having its intake connected via line **16'** to the bottom of sump **19** and its discharge to the upwardly disposed apex **10*a*'** of funnel **10'**.

It is, of course, practicable to separate the sump from the plating chamber, as by intermediate pipe connection, which can be desirable where the bath temperatures to be maintained in each are different.

Apparatus can be constructed from a wide variety of materials, such as Pyrex brand glassware, stainless steel, or stainless steel coated with a suitable corrosion-resistant polymer coating. Frequently, cleaning with nitric acid solution is desirable, and appropriate corrosion resistance must then be provided.

A specific apparatus constructed generally according to FIG. **1** utilized a frustoconical plating chamber **10** of 7 inches top diameter, the interior angle of the chamber being 48°. A 2 inch high cylindrical rim was adhered to the top of the funnel and this was provided with twelve ¼ inch dia. liquid overflow holes spaced equaly around the periphery.

The diameter of feed and outlet tubes was ⅜ inch i.d. and the pump **15** utilized was a Cole-Parmer 1/35 H.P. sealess magnetic drive centrifugal pump with polypropylene body and impeller. The elbow connecting with orifice **10*a*** was ¾ inch vertical dimension.

Except where otherwise indicated, the plating bath composition employed in the following examples was a standard DMAB (i.e., dimethylamine borane) reductant bath, as follows:

Nickel acetate	50	g./l.
Sodium citrate·$2H_2O$	25	g./l.
Lactic acid	25	g./l.
DMAB (i.e., dimethylamine borane) as reductant	2.5	g./l.
TDGA (i.e., thiodiglycolic acid) as stabilizer	0.1	g./l.
Santomerse S (commercial wetting agent	0.1	g./l.

The bath was prepared from a number of stock solutions which are numbered as follows for convenient reference:

Solution I	Nickel Acetate	62.5	g./l.
	Sodium Citrate	31.3	g./l.
	Lactic Acid	31.3	g./l.
Solution II	TDGA (i.e. thiodiglycolic acid)	20	g./l.
Solution III	Santomerse S	2	g./l.
Solution IV	DMAB (i.e., dimethylamine borane)	30	g./l.

To prepare 1 liter of plating solution, the sequence and amount of stock solutions added was as follows:

1. Heat 800 ml of Solution I to 55°C.
2. Adjust pH measured at room temperature to 6.5 by addition of reagent-grade NH_4OH.
3. Add 5 ml of Solution II.
4. Add 50 ml of Solution III.
5. Add 83 ml of Solution IV.
6. Add distilled water to bring bath volume to 1 liter.

Once prepared, the DMAB bath was operated under the following conditions:

1.	pH at room temperature	6.3 to 6.5
2.	Temperature	55°C.
3.	Area plating factor	5 to 10 sq.in./l.
4.	Bath replenishment was made at intervals of 1 hr.	

The bath-replenishment schedule was based on prior experimental work wherein wet chemical analysis of the DMAB and nickel ion concentrations were made during plating runs. The plating bath concentrations for each run were brought to standard levels during the "heat-up" period by making a wet chemical analysis and then adding the appropriate amounts of nickel ions, DMAB or TDGA.

For each run, the number of polymeric articles plated in the tumble plater (design of FIG. **1**) were the same. The acrylonitrile-butadiene-styrene **EP3510** articles consisted of five rectangles of dimensions ⅛ inch × ⅜ inch × ¾ inch, with a hole ⅛ inch diameter, ⅛ inch long, and a hole 1/16 inch diameter, ⅛ inch long, together with five rectangles of dimensions ⅛ inch × ⅜ inch × ¾ inch with a hole 1/32 inch diameter, ⅛ inch long, and a hole 1/64 inch diameter, ⅛ inch long. Finally, there were five glass-filled polymer articles (acrylonitrile-butadiene-styrene AF–1004) with appropriate dimensions of ¾ inch × ⅜ inch × ⅜ inch having a hole 3/64 inch diameter, ¼ inch long, intersecting at right angles with a hole 0.028 inch diameter, ⅛ inch long. The articles were first taken through the standard polymer preplate line hereinbefore described.

Wherever a "tumble plater" is referred to in this description, it will be understood that article tumbling was conducted, regardless of whether the plating solution contained suspended solids or not.

The tumbling in the reported Examples was gentle in nature, involving five or six end-over-end rotations per minute of single articles, as observed with a stop watch. However, the tumbling rate can, of course, be varied broadly to suit particular requirements.

EXAMPLE 1

One lot of specimens as described was taken from the polymer preplate line and placed for 10 mins. in a 4-

liter beaker which contained a standard DMAB plating bath, with gentle agitation being provided to the parts by manually imparting an up-and-down motion to the stainless steel basket in which they were contained. The specimens, plated with a thin nickel strike, were then transferred by dumping from the basket into the plating chamber of the tumble plater (FIG. 1), which also contained the standard DMAB plating bath. Plating ensued for 1 hr. in this bath, free of any hard-particle additions. Then a quantity of αAl_2O_3 of hexagonal crystal structure and an equiaxed shape with average particle size of 0.3μ was introduced into the tumble plater from a blended suspension of these particles in a separate beaker containing the DMAB plating bath. Over a period of 3½ hr., 90 g. of αAl_2O_3 was added to the bath at hour intervals in 30 g. increments. Since the final tumble-plater bath volume was 6 liters, the αAl_2O_3 loading factor at the end of the run was 15 g./l.

Metallographic and X-ray examination confirmed the presence of composite αAl_2O_3-electroless Ni–B deposit on the polymer substrates. Also, metallographic examination confirmed the presence of a composite coating in all hole diameters. Quantimet analysis (i.e., the Quantimet Image Analyzing Computer marketed by Metals Research, Ltd., Hertz, England) indicated that 13.1 vol. percent of αAl_2O_3 was present in the composite layer. Yarn-line wear testing by running in contact with a coated specimen a 15-denier dull nylon monofilament with conditions of 5° break angle 10 g. load, and 1,000 yd./min. travel velocity indicated that the wear after 10 mins. was 0.113×10^{-6} cm^3 or 0.678×10^{-6} cm^3/hr.

EXAMPLE 2

A second lot of specimens was taken from the polymer preplate line and placed for 10 mins. in a 4-liter beaker which contained the standard DMAB plating bath. Gentle agitation was provided to the parts by manually imparting an up-and-down motion to the stainless steel basket in which they were contained. The specimens were then emptied from the stainless steel basket into the tumble plater (FIG. 1 design) and allowed to plate for 1 hr. in this bath. The tumble plater bath was the same one as used in Example 1, except that it had been carefully filtered at the end of the preceding fun in order to remove any suspended hard particles. At the end of the 1-hr. plating period, αAl_2O_3 of hexagonal crystal structure and an acicular shape with average particle size of $20 \times 10\ \mu$ was introduced into the tumble plater. Over a period of 4½ hrs., 12 g. of αAl_2O_3 was added to the bath at half-hour to hour intervals in 1.2 g. or 2.4 g. increments.

Metallographic and X-ray examinations confirmed the presence of a composite αAl_2O_3 — electroless Ni-B deposit. Also, metallographic examination confirmed the presence of a composite coating in all hole diameters. Quantimet analysis indicated that 10.1 vol. percent of αAl_2O_3 was present in the composite layer. Yarn-line wear testing for a period of 6 hrs. using 15-denier dull monofilament with conditions of 5° break angle, 10 g. load, and 1,000 yd./min. running velocity indicated that the wear was 0.0163×10^{-6} cm^3/hr. Since the tumble plater bath volume was 6 liters, the αAl_2O_3 loading factor at the end of the run was 2 g./l.

EXAMPLE 3

A third lot of specimens was taken from the polymer preplate line and then placed in a 4-liter beaker which contained the standard DMAB plating bath for 10 mins. Gentle agitation was provided to the parts by manually imparting an up-and-down motion to the stainless steel basket in which they were contained. The specimens were then emptied from the stainless steel basket into the tumble plater (FIG. 1 design) and allowed to plate for 1 hr. in this bath. The tumble plater bath was the same one used in Example 2, except that it had been carefully filtered at the end of the preceding run in order to remove any suspended hard particles. At the end of the 1-hr. plating period, acicular rutile (TiO_2) of tetragonal crystal structure, and with a fiber diameter of 0.2 microns and a fiber length of 3 microns, was introduced into the tumble plater. The addition was 6 g., corresponding to a loading factor of 1 g./l. The composite plating period was 3½ hrs.

Metallographic and X-ray examination confirmed the presence of a composite acicular rutile-Ni-B deposit. Also, metallographic examination confirmed the presence of a composite coating in all hole diameters. Quantimet analysis indicated that 3.4 vol. percent of acicular rutile was present in the composite layer. Yarn-line wear testing for a period of 1 hr. using 15-denier dull monofilament with conditions of 5° break angle, 10 g. load, and 1,000 yd./min. running velocity indicated that the wear was 0.196×10^{-6} cm^3/hr.

EXAMPLE 4

A small wear article fabricated from glass-filled AF–1004 polymer was formed with an injection molded flared entrance through slot measuring 7 mils wide × 40 mils long × 200 mils deep.

The article, after the hereinbefore described polymer pretreatment, was coated by the following procedure, using the apparatus of FIG. 1:

a. one hour of electroless tumble plating in the standard DMAB plating bath, free of particulate additions,

b. 3½ hours of electroless tumble plating in the standard DMAB plating bath containing 2 g./l. addition of suspended 9μ dia. diamond particles, and

c. 2 hours of electroless plating in a conventional magnetic-stirred beaker containing standard DMAB plating solution, free of particulate additions, this last step being added to provide metallographic edge protection.

A micrograph sectional plan view taken at the 100 mil level clearly showed an extraordinarily uniform coating over the slot walls of about 2 mil thickness, throughout which 9μ diamond particles were uniformly dispersed. This example illustrates the excellent "throwing power" capability of the invention method, particularly for plating the interiors of small holes and slots.

EXAMPLE 5

The following Table II reports a number of different plating runs made according to this invention in apparatus of FIG. 1 indicating composite dependence on particle size and also on particle nature (e.g., Ni-B baths were not effective to lay down titanium diboride or tungsten carbide on the polymer substrates involved and in the case of Ti metal a composite was not obtained in all areas).

All baths were of the Ni-B type, except the last reported, which was a commerial Ni-P type, marketed by the Shipley Co., Boston, Mass.

TABLE II

Description of Article					
Substrate Material	Holes or Cavities	Particulate Material	Total g./l.	Particle Size and Shape	Remarks
		Al_2O_3	2	equiaxed 0.3μ	no composite observed
EP 3510 polymer (size and shape ¾" × ⅜" × ⅛")	⅛", 1/16" 1/32", and 1/64" diam. holes ⅛" deep	Al_2O_3	5	equiaxed 0.3μ	composite coating all areas, 9.1 vol. %
		Al_2O_3	15	equiaxed 0.3μ	composite coating all areas, 13.1 vol. %
		Al_2O_3	0.1	acicular 20μ × 10μ	low loading of particles on surface; no composite in 1/64" hole
and		Al_2O_3	2	acicular 20μ × 10μ	composite coating all areas, 9.6 vol. %
AF-1004 glass-filled polymer (size and shape approximately ¾" × ⅜" × ⅜")	3/64" and 1/32" hole intersecting at 90°; open-ended cavity 200 mil × 40 mil × 7 mil	TiO_2	1	acicular 0.2μ × 3μ	composite coating all areas, 3.4 vol. %
		TiO_2	15	acicular 0.2μ × 3μ	composite coating all areas
		diamond	2	equiaxed 9μ	composite coating all areas
		$MoSi_2$	2	equiaxed 1–20 μ	composite coating all areas
		BN	2	equiaxed 1–10 μ	composite coating all areas
EP 3510 polymer (size and shape ¾" × ⅜" × ⅛")	⅛", 1/16", 1/32", and 1/64" diam. holes ⅛" deep	Ti	2	equiaxed 1–5 μ	no composite observed
		Ti	10	equiaxed 1–5 μ	composite observed in some areas
and		SiC	2	equiaxed 1–10 μ	composite coating all areas
AF-1004 glass-filled polymer (size and shape approximately ¾" × 154" × 154")	3/64" and 1/32" hole intersecting at 90°; open-ended cavity 200 mil × 40 mil × 7 mil	TiB_2	2	equiaxed 1–10 μ	no composite; plating on particles
		WC	2	equiaxed 1–10 μ	no composite; plating on particles
		Al_2O_3	2	acicular 20 × 10 μ	composite coating on exterior surfaces; no composite in 1/64" hole

Other designs of apparatus adapted to conduct plating in sequential stages, or continuously (as contrasted with batch-wise in FIGS. **1** and **2**) are shown in FIGS. **3–5**, inclusive.

Thus, FIGS. **3A** and **3B** illustrate a series arrangement comprising three funnel-type platers **22, 23** and **24**, connected at their upper ends in order from right to left, so that articles **25** to be plated can be impelled in sequence from one plater to the next by appropriate manipulation of valves **26** and **27** after preselected residence times in each plater. In the interim, with valves **26** and **27** turned down, pump **28** is operated to recirculate plating solution continuously via lines **32** and **33**, without transfer of the articles, but, of course, maintaining tumbling at all times.

Finally, articles **25** are caught on screen **30,** mounted across the outlet **24***a* of plater **24**, from which they can be removed at will while the plating solution is recycled via line **31** connected to the intake of pump **28.**

A somewhat similar design is depicted in FIG. **4**, the platers **38–38***d* being, in this instance, trough-like in form and generally V-type in longitudinal cross-section.

Weirs **39***a* and **39***d*, preferably of slightly decreasing height in the order recited, define the individual plater stages. A single pump **40** discharges into a common manifold **41** which is provided with individual discharge jets **42***a* and **42***d*, inclusive, servicing individual platers. Transfer of articles from one plater to the next in sequence is readily effected by periodic manual manipulation of the individual valves **43***a*–**43***d*, inclusive.

The terminal compartment, **38***e*, serves merely as a collector for articles **45** having finished plate coatings, automatic article removal being obtained by an inclined, cleated belt conveyor **44,** which is intermittently operated by a motor (not shown) to carry the articles out to a suitable finished-product collector.

Compartment **38***e* is provided with an inclined funnel bottom **46,** covered with a sloped screen **47,** through which plating solution is immediately withdrawn via pump intake line **48,** so that suspended particles have no opportunity to settle out during solution recycle.

A modification in this design entails cutting vertically oriented alternately arranged slots in weirs **39***a*–**39***c* (with, optionally, a shallower slot in weir **39***d*), so that there is continuous flow of plating solution and articles being plated through the apparatus. This has the disadvantage that certain articles might dwell longer within given plating cells than others, with corresponding variation in plating coats. However, acceptance by visual inspection cures this difficulty.

FIGS. 5A and 5B show a single funnel continuous plater **53** provided with a spiral baffle **54** defining a continuous plating path from the outside periphery to the center.

Baffle **54** is open at the bottom, so that a single jet **55** connected to the funnel apex **53***a* provides tumbling action throughout the entire plating path. Discharge of plating bath solution (and articles **57**) is effected via drain connection **56** communicating with the terminal center of baffle **54**.

Articles **57** are caught on screen **58** covering the exit end of sump funnel **59**, whereas plating solution is recycled from the outlet end **59***a* via pump intake line **60** through centrifugal pump **61** back into the plater via jet **55**.

Articles to be plated are supplied to the outside periphery of the plater by gravity feed through an inclined pipe chute **65**.

Numerous other specific designs of apparatus can be provided to suit special requirements, utilizing the general principles hereinbefore elaborated with reference to FIGS. **1–5**, inclusive.

What is claimed is:

1. Apparatus for concomitant particulate deposition in electroless plating comprising, in combination, a vertically oriented frusto-conical vessel, an electroless plating solution pump connected with discharge port in communication with the small diameter end of said frusto-conical vessel, a receiving vessel connected in open fluid communication with the large end of said frusto-conical vessel, and means connecting said receiving vessel to the intake side of said pump.

2. Apparatus for concomitant particulate deposition in electroless plating according to claim **1** of articles having a density greater than the specific gravity of said plating solution wherein said frusto-conical vessel is oriented vertically with large end up.

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