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# PROCESS OF PLATING METAL OBJECTS

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## ABSTRACT OF THE DISCLOSURE

Conductive substrates, especially the surfaces of small ferrous metal parts, are galvanomechanically plated by contacting their exposed surfaces with a free-flowing liquid containing the dissolved salt of a plating metal, together with a driving metal which is less noble than either the substrate or the plating metal. The driving metal is desirably particulate and the process is especially adapted for use in a conventional tumbling barrel.

This invention relates to the metal plating of conductive substrates. More particularly, the invention relates to a new and useful means for metal plating which is more convenient and less expensive than electroplating, which provides thicker coatings than can be obtained by displacement plating, and which preserves the simplicity of mechanical plating.

Two major techniques are known by which metal parts are provided with resistant coatings of another metal—electroplating and mechanical plating. In electroplating, an external direct current voltage is applied to two electrodes immersed in an electrolyte containing ions of the metal to be plated out, the cathode constituting the part which is to be plated.

In mechanical plating articles to be plated are placed in a tumbling barrel, together with particles of the plating metal and promoter chemicals, preferably, in an aqueous solution containing impact media. As the tumbling barrel is rotated or otherwise agitated, the plating metal particles are flattened and cold-welded to one another and to the surface of the articles by the mechanical hammering of the impact media and the articles to be plated to provide the articles with visually continuous platings.

I have now discovered that by utilizing a proper combination of metal powder and water-soluble metal salt, metal plating results which incorporates many of the advantages of electroplating without the requirement of heavy investments for electrical and other equipment while preserving the simplicity, convenience and economies of mechanical plating. In accordance with this invention, a composition of a "driving," or plating inducing, metal and an ionizable salt of a metal to be plated are introduced into a liquid medium in which the salt is soluble, which liquid medium is in contact with an electrically conductive substrate. Then, upon contact, as by mechanical agitation or otherwise, of the substrate to be plated with the driving metal, the plating metal deposits from solution onto the substrate and provides a smooth, uniform coating layer of any desired thickness.

Since no external current source is necessary, and since the process works with simple mechanical procedures to provide coating deposited with the uniformity of electroplated coatings, an entirely new means for applying metal coatings or platings is provided herewith.

In the practice of the process the substrate to be plated may be a massive metal article, or small parts such as washers, hose clamps, screw fasteners, etc., or it may be itself a metal powder, the flakes or granules of which are to be plated. In any event, the driving metal must be less



noble, i.e. more active electrochemically in the solution in which it is suspended or with which it is contacted, than either the plating metal (provided by the metal salt) or the metal substrate to be plated.

In many instances this invention provides for producing a superior protective or decorative metal plating which is a finished product per se, directly on a conductive substrate. The invention is also particularly useful in the preplating of small ferrous metal parts with tin prior to electrically or mechanically plating them with zinc, cadmium, or other corrosion-resistant metal. One specific product contemplated by this invention is a novel storable product which can be used to impart a uniform smooth metal plating to electrically conductive parts.

While the extent of utility of this new plating system is yet to be determined, it has solved a long-existing problem in applying pre-plating or strike coatings (coatings for the anchoring of subsequent metal platings) to ferrous metal substrates, particularly in mechanical plating operations. Heretofore, a common pre-plating material for ferrous metal parts has been copper, applied either by electroplating or by displacement plating. In mechanical plating, displacement plating is generally used to apply strike coatings of only covering thickness; as a practical matter, such coatings are limited to copper.

Although copper is generally satisfactory as a pre-plating metal in mechanical plating operations, there are environments, e.g., certain gaseous environments, wherein copper platings (even copper undercoatings) are undesirable because of the polymer-inducing catalytic effect of the copper. Also, copper suffers from the disadvantage that its natural reddish color and its oxidized black color contrast with that of the final plating. Thus, the copper sometimes "shines through" a subsequently applied plating, which then may appear mottled or off-color, even though the functionality of the plating is not impaired. Silvery pre-plating metals, such as tin, cadmium, lead, nickel, mercury, silver, and thallium virtually eliminate complaints based on appearance of the finally plated article.

Tin has been recognized as an excellent pre-plating material, and is sometimes applied by electroplating, but it is much more difficult to apply by displacement plating than is copper. If the tin plating bath is acidic, it is hard to obtain satisfactory coatings unless extremely high temperatures are used; even then plating is slow and erratic, and hydrogen embrittlement often occurs. If the tin plating bath is alkaline, either the normally acidic cleaning bath (which precedes plating) must be neutralized or the parts must be removed from the bath; besides, alkaline tin plating baths require an unduly high concentration of tin salt.

As noted previously, in accordance with this invention a metal or other electrically conductive substrate is plated by contacting the substrate with a free-flowing liquid containing ions of a dissolved salt of the plating metal, the operation being carried out in the presence of a "driving" metal which is less noble than either the substrate or the plating metal. Preferably the driving metal is employed in finely divided form and the liquid is subjected to continuous agitation during plating, so that the driving metal particles contact substantially the entire surface to be plated. Although this plating operation can be carried out simply and readily in almost any available container which has an electrically insulating lining, it is particularly adapted for use in tumbling barrels especially where the barrel is simultaneously rotated and axially reciprocated.

The plating procedure appears to be electro-mechanical in nature, a simple cell being formed as the plating inducing driving metal is brought into mechanical contact with the surface of the conductive substrate. Plating is facilitated by adjusting the pH of the solution so that the driving metal is rendered more soluble, the potential difference between the driving metal and the plating metal also promoting solution of the driving metal. As the plating inducing metal tends to go into solution, it releases electrons, which then reduce the positively charged ions of the plating metal, causing the plating metal to deposit on the substrate.

When the driving metal is provided as a solid metal powder in the plating solution, agitation of the solution causes the metal particles to contact all of the substrate surfaces exposed to the liquid, even where the surface geometry is quite intricate. Thus, in this respect the plating continuity is on the order of completeness of displacement coatings, but, unlike displacement plating, it is not limited to extremely thin coatings. This new electromechanical system should enable plating the interior of tubing substantially uniformly throughout its length.

My invention will be better understood upon referring to the following illustrative but non-limitative examples, in which all parts are by weight unless otherwise noted.

### Example I

The following ingredients were placed in a 4-quart open-end tumbling barrel:

| | | |
|---|---|---|
| Glass beads (range from 4 mm. to about 0.1 mm.) | grams | 3500 |
| $SnCl_2$ | do | 3.0 |
| Alcoa "123" aluminum powder | do | 6 |
| "Versene 100" | do | 2 |
| $NaHSO_4$ sufficient to lower pH to approximately 2. | | |
| Previously cleaned 3/8-inch cold-rolled steel washers | grams | 5000 |
| Water | liters | 1½ |

The Alcoa "123" powder, which is the driving metal, has a particle size in the range of approximately 5 to 40 microns. "Versene 100," the disodium salt of ethylene diamine tetraacetic acid, although not absolutely necessary, appears to improve adhesion of subsequently applied platings. The glass beads constituted impact media.

The tumbling barrel (which was still hot from steam cleaning the parts) was then rotated at 50 r.p.m. for approximately 10 minutes, after which the liquid was dumped out of the barrel and the washers rinsed and examined. It was apparent that they had received a thin uniform tin plate, the satisfactory adherence of which was established by pressing the adhesive surface of a tacky and pressure-sensitive adhesive tape into uniform contact with the surface and removing it without stripping off any of the plated metal. When subsequently mechanically plated with zinc, the washers displayed significantly greater corrosion resistance than washers which had been identically zinc plated over a conventional displacement deposited copper pre-plate.

When Example I was repeated with the aluminum powder omitted, no tin plating whatsoever was detected.

Generally speaking, the smaller the particle, the less the total weight of driving metal required. On the other hand, small aluminum particles are particularly susceptible to oxidation and may provide a smaller amount of aluminum for a given weight of powder. Large driving metal particles can be used, but if the size becomes too great, the particles are unable to penetrate into some of the crevices in intricate parts; additionally the larger particles more quickly acquire a displacement-plated layer of the plating metal than do smaller particles. Ideally the composition should be balanced so that the amount of metal powder is just sufficient to supply the number of electrons to reduce all the metal salt ions. If too great an excess of the metal powder is present, the powder itself tends to be displacement-plated with the metal of the metal salt. I have found that approximately 4 to 8 grams (0.15–0.30 gram mol) of 10-micron aluminum particles functions effectively with 3 grams of $SnCl_2$ (i.e., approximately 1.9 grams, or 0.016 gram mol, of tin).

The optimum composition in a given situation should be modified in view of densities, materials, molecular weights, plating thickness, and so on. For example, if the pre-plating metal salt has a lower molecular weight than $SnCl_2$, or if the metal has a valence greater than 2, more aluminum will be necessary. If a powdered metal having a less tenacious oxide coating than aluminum is employed, the amount of powder may be decreased. If, on the other hand, the powdered metal has a valence lower than aluminum, more atoms of metal will be required to yield the same number of electrons. Empirically, I have found that where 2–5 micron zinc powder is used instead of 10-micron aluminum powder, the weight necessary is only about one half as great.

By replacing the $NaHSO_4$ with NaOH to provide an alkaline solution having a pH of about 11–13, and by replacing the $SnCl_2$ with $K_2SnO_3$ to provide the same amount of available tin, results generally similar to those just described relative to the acid system have been obtained. While aluminum requires an environment which is either fairly strongly acidic or fairly strongly alkaline to function well as a driving metal in the practice of my invention, metals which have less tenacious oxides do not require such aggressive pH conditions. Numerous other metals which rank above both tin and iron in the electromotive series can also be used as the driving metal, as the following examples illustrate.

### Example II

The following ingredients were mixed in a 400 ml. beaker:

| | | |
|---|---|---|
| $SnSO_4$ | grams | 2 |
| Manganese powder (−200 mesh) | do | 1 |
| Glass spheres (5/32-inch) | do | 200 |
| $H_3PO_4$ (85%) | cc | 1 |
| Water, 150° F. | cc | 50 |

A previously cleaned 3/8-inch steel washer was dropped into the preceding composition, which was then stirred vigorously for approximately 1 minute. Upon removal, the washer was found to have a uniform thin tin plating. When the identical composition was employed, except for omitting the manganese powder, no coating whatsoever was obtained.

### Example III

Example II was repeated except for the substitution of 1 gram of powdered magnesium (−100 mesh) for the manganese and $SnCl_2$ instead of $SnSO_4$. Results were essentially the same.

### Example IV

Example III was repeated, except that 1 gram of −325 mesh titanium was substituted for the powdered magnesium and a few drops of HF were added to help remove the oxide from the titanium particles. Results were substantially identical.

### Example V

Example II was repeated, except that 1 gram of −325 mesh zinc was substituted for the powdered maganese. Results were substantially identical.

### Example VI

To a 400 ml. beaker the following ingredients were added:

| | | |
|---|---|---|
| CdO | grams | 2 |
| −200 mesh aluminum particles | do | 1 |
| Hydrochloric acid (12 N) | cc | 2 |
| Water, 150° F. | cc | 50 |
| Glass spheres media (5/32-inch) | grams | 200 |

A 3/8-inch cold rolled steel washer was dropped into the composition, which was then stirred vigorously for one minute. A thin, uniform cadmium plating resulted.

### Example VII

A 3/8-inch cold rolled steel washer was cleaned in 50 ml. of a solution consisting essentially of phosphoric acid and a mixture of surfactants. To a beaker containing the solution and the washer were then added 2 grams of lead fluoborate and 1 gram of —325 mesh zinc. The composition was stirred for one minute, after which time it was observed that a lead coating had formed on the washer.

### Example VIII

Example VII was repeated except that 1 gram of $HgCl_2$ was substituted for the lead fluoborate. A mercury coating formed on the surface of the washer.

### Example IX

Example VII was repeated except that 1 gram of silver nitrate was substituted for the lead fluoborate. A silver coating was formed on the washer.

### Example X

Example VII was repeated except that 1 gram of thallium chloride was substituted for the lead fluoborate. A thallium coating was formed on the washer.

### Example XI

The following ingredients were placed in a 400 ml. beaker:

| | | |
|---|---|---|
| $SnCl_2$ | grams | 1 |
| $NaHSO_4$ | do | 7 |
| Water, 150° F. | cc | 50 |
| Zinc particles (—325 mesh) | grams | 1 |
| Glass spheres (3/32-inch) | do | 200 |

A 2" x 4" x 1/16" copper template was then used to stir the solution vigorously for approximately one minute, at the end of which time a tin coating was formed on the template.

### Example XII

Example XI was repated except for the substitution of a 2" x 2" x 1/16" molybdenum template for the copper. Results were substantially identical.

### Example XIII

Example XI was repeated except for substitution of a brass template for the copper. Results were substantially identical.

### Example XIV

The following ingredients were placed in a 400 ml. beaker:

| | | |
|---|---|---|
| $NiCl_2$ | grams | 1 |
| Aluminum powder | do | 2 |
| $H_3PO_4$ (85%) | cc | 1.5 |
| $H_2O$, 150° F. | cc | 50 |

A previously cleaned 3/8-inch steel washer was dropped into the composition, which was then stirred vigorously for about 1 minute. Upon removal, the washer was found to have a uniform nickel plating.

The preceding examples demonstrate the effectiveness of using a powdered driving metal in the plating systems described. Powdered metal has the advantage that it is able to penetrate small nooks and crannies and provides substantially complete coverage and contact with the surface which is to be plated. A large coil of sheet steel may, however, be continuously plated, e.g., tin-plated, by passing it under and against a roller made of the driving metal, e.g., an aluminum roller, while flooding the surface with a solution of a salt of the plating metal.

When aqueous treating solutions are employed, the driving metal is preferably chosen from other than Group I–A or II–A of the Periodic Table (especially the former), although even these alkali metals may be of use, e.g., in an ionizing solvent with which they do not react violently.



The relative positions of the metal of the part and the metal of the salt which is to be plated in the electromotive series do not seem to be especially critical, but, in any event, the plating inducing metal is less noble (or more active) than either of the other two. The difference in oxidation potential between the plating inducing metal and the substrate apparently need be only that necessary to overcome the resistance of the electrical circuit set up.

Where either the substrate or the driving metal is significantly more active electrochemically than iron, the pH of the plating bath should be controlled to minimize dissolving the part being plated, the plating, or both. For example, if iron is to be plated with zinc, using powdered magnesium as a driving metal, the pH of the plating bath should probably be at least 2.

The principles taught herein are subject to numerous variations and adaptations other than those specifically mentioned. For example, a porous mechanically zinc plated part may be "sealed" by tumbling it in an acidified solution of a tin salt containing dispersed aluminum particles. The driving metal may advantageously be an alloy (e.g., Al:Mn, 95:5 Al:Zn, 45:50:5 Sn:Al:Zn, and many others) rather than a single metal. In fact, the use of such alloys may permit a reduction of the amount of acid required in the solution, the presence of even minor amounts of other metals apparently reducing the tenacity with which oxide is normally attached to metals like aluminum.

While driving metal particles and the plating metal salt may be added to the liquid individually, these materials are preferably combined in solid form in a predetermined ratio to provide the most efficient plating coverage for the surface to be plated. Thus, the driving metal particles may be pre-mixed with inhibitor (e.g., 1 or 2 drops of diethanolamine or n-tallow 1,3-propylene diamine per gram of 10-micron aluminum powder), and the salt of the plating metal and the mass pressed into a pellet. Still another way is to disperse the metal powder in a solution of water-soluble gum (e.g., 5 grams of 2–5 micron zinc particles in 10 cc. of a 5% aqueous solution of hydroxy ethyl cellulose), evaporate the water, and crush the resultant cake, leaving metal particles surrounded with a thin water-soluble gum layer. The gum-encased metal particles, the salt, and other ingredients, may then be pressed into a single cake or incorporated in a textile or abrasive product for subsequent use in the presence of water.

What I claim is:

1. A galvanomechanical process for plating a thin continuous layer of silvery metal on each of a number of small metal parts, comprising the steps of

providing in a tumbling barrel
- water,
- said metal parts,
- impact media,
- a water-soluble salt of said silvery metal,
- a small amount of a powdered driving metal which is less noble than either said silvery metal or the metal of said parts, and
- an agent which will render the pH of the liquid barrel contents such as will dissolve the driving metal, and

rotating said barrel to agitate the contents thereof exposed to the atmosphere, whereby the metal parts are contacted, substantially over their entire exposed surfaces and including such difficultly accessible areas as thread roots, by the remaining contents of said barrel for a brief time on the order of ten minutes or less.

2. The process of claim 1 wherein said parts are made of ferrous metal.

3. The process of claim 2 wherein the silvery metal is silver.

4. The process of claim 2 wherein the silvery metal is nickel.

5. The process of claim 2 wherein the plating metal is thallium.

6. The process of claim 2 wherein the plating metal is mercury.

7. The process of claim 2 wherein the plating metal is cadmium.

8. The process of claim 2 wherein the plating metal is tin.

9. The process of claim 2 wherein the plating metal is lead.

10. The process of claim 2 wherein the driving metal is zinc.

11. The process of claim 2 wherein the driving metal is aluminum.



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# REEXAMINATION CERTIFICATE (96th)


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**Golben**

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[54] **PROCESS OF PLATING METAL OBJECTS**


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[52] **U.S. Cl.** .................. **427/242;** 106/1.05; 106/1.29; 204/Dig. 10

[58] **Field of Search** .......................................... None


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[57] **ABSTRACT**


Conductive substrates, especially the surfaces of small ferrous metal parts, are galvanomechanically plated by contacting their exposed surfaces with a free-flowing liquid containing the dissolved salt of a plating metal, together with a driving metal which is less noble than either the substrate or the plating metal. The driving metal is desirably particulate and the process is especially adapted for use in a conventional tumbling barrel.

## REEXAMINATION CERTIFICATE ISSUED UNDER 35 U.S.C. 307.

NO AMENDMENTS HAVE BEEN MADE TO THE PATENT.



AS A RESULT OF REEXAMINATION, IT HAS BEEN DETERMINED THAT:

Claims **1-11** having been finally determined to be unpatentable, are cancelled.

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