

[54] **COPPER PLATING ON ZINC AND ITS ALLOYS**

[76] Inventor: **Darwin P. Jensen**, 2565 Palos Verdes West, Palos Verdes Estates, Calif. 90274

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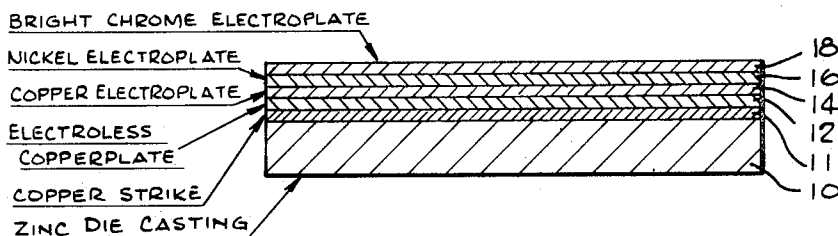
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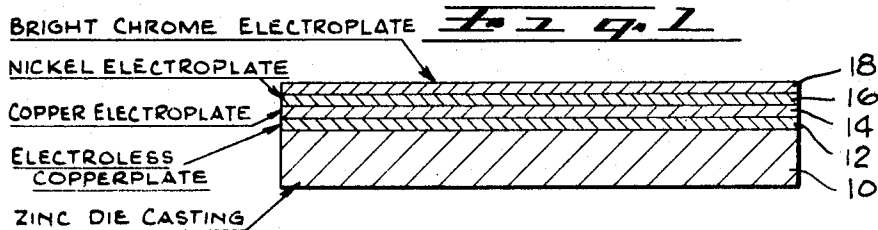
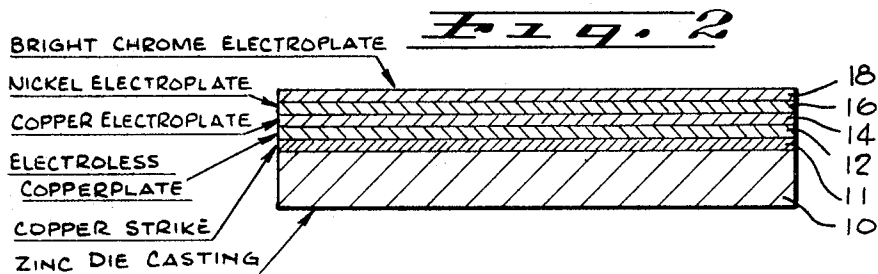
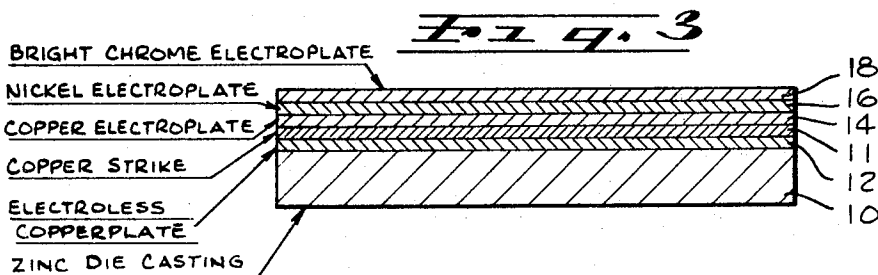
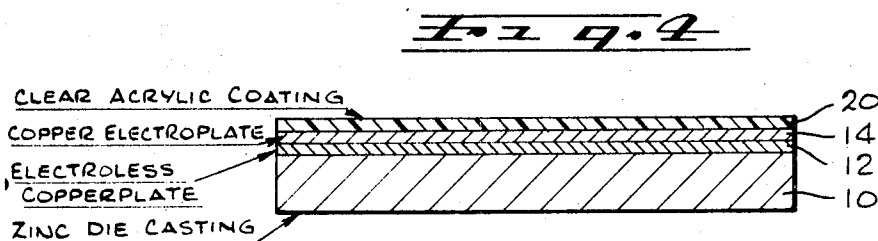
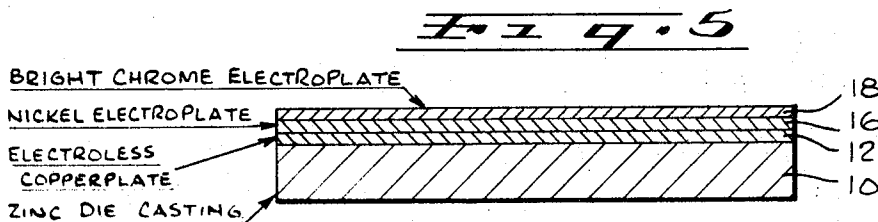
*Primary Examiner*—John H. Mack  
*Assistant Examiner*—R. L. Andrews  
*Attorney*—Max Geldin

[57] **ABSTRACT**

Production of a uniform, continuous corrosion resistant bonded copper coating on a zinc or zinc alloy body, by a process which comprises contacting the zinc or zinc alloy body with an electroless copper plating composition or solution consisting essentially of a soluble copper salt, e.g., copper sulfate, a complexing agent, e.g., citric acid, and a reducing agent, e.g., sodium hypophosphite. The resulting zinc or zinc alloy body can then be contacted with a copper electroplating bath, and according to one embodiment the resulting copper plated zinc or zinc alloy body is then treated in a nickel electroplating solution, followed by treatment in a chromic acid electroplating solution, to provide a corrosion resistant bright attractive metal coating on the zinc or zinc alloy body. The above noted novel electroless copper plating composition, and the zinc or zinc alloy article coated with an electroless copper plating.

**17 Claims, 5 Drawing Figures**





INVENTOR.  
DARWIN P. JENSEN

BY *Max Nelson*

ATTORNEY

## COPPER PLATING ON ZINC AND ITS ALLOYS

This invention relates to metal deposition or plating, and is more particularly concerned with the provision of procedure for plating zinc or its alloys, particularly zinc die casting, with a copper coating, employing an electroless copper plating solution, preferably followed by application of electroplated nickel and electroplated chrome coatings, to provide a corrosion resistant and attractive metal coating on the zinc or zinc alloy body, with the provision of novel electroless copper plating compositions employed in such procedure, and the plated zinc or zinc alloy article containing an electroless copper coating produced according to the invention process.

Electroless metal deposition refers to the chemical deposition of an adherent metal coating on a conductive, non-conductive, or semi-conductive substrate, e.g., a metal, in the absence of an external electrical source, as contrasted to electroplating, which involves electrolytic plating by the application of an external electrical current. Electroless metal deposition is often employed to provide a metal base or coating suitable for subsequent electroplating thereon.

Zinc die casting is used extensively for the production of commodities including plumbing fixtures, door handles, toys such as slot racers, and the like. However, zinc die casting tends to oxidize and corrode readily and form an undesirable powdery surface or salt layer, resulting in deterioration of the zinc base metal and formation of an unsightly surface appearance with age. Accordingly, it is usual practice to electroplate copper on such zinc die casting, the advantage of copper plating as contrasted for example, to plating with noble metals such as gold, platinum, and the like, being of course its economy.

Conventional procedure for electrolytically plating copper on zinc or its alloys, particularly zinc die casting, generally includes first treating the zinc or zinc die casting in an electroplating solution generally termed a copper strike solution, e.g., containing copper cyanide, then treating the zinc or zinc alloy part in a bright acid copper electroplating bath to form a copper electroplate, the part then usually being treated in an electroplating nickel bath, followed by treatment in a bright chrome electroplating bath, to provide nickel and chrome overcoats on the electroplated copper coating.

However, several problems are presented in the above noted conventional procedure for copper plating zinc or its alloys such as zinc die casting. Thus, any bare zinc spots which are not electroplated with copper in the initial copper electroplating solution, that is the copper strike solution, tends to poison the subsequent bright copper electroplating bath and also the following nickel and chrome acid electroplating baths when the zinc or zinc alloy is treated therein. This results in delay and expense in replenishing or replacing these poisoned baths, and also in the rejection or retreatment of the defective zinc or zinc alloy parts. It has been found from experience that the presence of bare zinc spots on the zinc or zinc alloy parts often occurs following treatment in the initial copper electroplating strike solution, e.g., cyanide strike, regardless of the care taken during this initial copper electroplating step. This not only results in the above noted poisoning of subsequent electroplating baths, but where such bare spots are present following treatment in the copper strike,

the copper coating from the strike and adjacent such bare spots will promote galvanic corrosion at the bare zinc-copper interface, resulting in an inferior zinc or zinc alloy part.

Although heretofore it has been considered difficult and impractical to apply an electroless copper plating to zinc or its alloys, e.g., zinc die casting, generally due to the high reactivity of zinc in relation to the more noble metals such as copper, it has now been found according to the present invention that an improved electroless copper coating can be applied to zinc and its alloys such as zinc die casting, by treating such zinc or zinc alloy part in a novel electroless copper plating bath, as described more fully below, to provide a uniform continuous bonded copper coating, essentially without leaving any bare zinc spots, and on which a subsequent copper electro-plate can be applied, followed, if desired, by nickel and chrome electroplate overcoatings, to afford complete coverage of the zinc or zinc alloy substrate by the metal plating, the uniform copper coating applied by treatment in the electroless copper plating bath providing protection against poisoning of subsequent plating baths, and resulting in improved corrosion resistance of the metal plating system.

Briefly, the essential feature of the invention process is the production of a uniform continuous bonded electroless copper coating on a metal body selected from the group consisting of zinc and its alloys, by contacting such metal body with an electroless copper plating composition or solution consisting essentially of a soluble copper salt, a complexing agent, and a reducing agent, to form such electroless copper coating on such metal body, prior to treatment of such metal body in a subsequent metal, preferably copper, electroplating bath.

The invention procedure can be employed for providing an improved copper plating, and/or improved copper-nickel-chrome plating on substantially pure zinc, and also the various zinc alloys, particularly zinc die casting, which is a zinc alloy containing about 90 to about 96 percent zinc, some of such zinc die casting alloys containing 4 to about 5 percent aluminum, and some of such alloys containing both aluminum and copper, e.g., about 1 to about 5 percent copper and about 3 to about 5 percent aluminum. Specific zinc alloys to which the invention procedure is applicable include:

A. zinc alloy containing 4.0% Al, 0.05% Mg, (all others 0.22% max.)

B. zinc alloy containing 4.0% Al, 0.05% Mg, 1.00% Cu

C. zinc alloy containing 4.0% Al, 0.05% Mg, 3.00% Cu

Substantially pure zinc, e.g., 99 to 99.99 percent zinc, with small amounts of impurities such as Pb, Fe and Cd, can also be treated according to the invention. It will be understood however, that zinc alloys other than those set forth above can be treated in accordance with the invention principles.

According to one mode of procedure for practicing the invention, the zinc or zinc alloy part, e.g., a zinc die casting, preferably is first cleaned by treatment with one or more cleaning agents which can include, for example, treatment in a degreaser, such as 1,1,1-

trichloroethane or trichloroethylene, followed by treatment in an alkaline cleaner such as aqueous trisodium phosphate which can contain a wetting agent or surfactant, or in an anodic cleaner such as one containing tetrasodium pyrophosphate and borax, followed by treatment in an alkaline zincate solution, to remove surface dirt and soils from the part, and, if desired, followed by a mild acid dip, e.g., an aqueous 2 to about 10 percent citric acid solution. It will be understood that any one or more of the above noted cleaning treatments can be employed as desired, depending upon the condition of the surface of the zinc or zinc alloy part, to provide the part with a clean grease-free surface, which is also free of surface oxides or zinc salts. The time and temperature of treatment in the various pretreatment or cleaning baths noted above can be varied as is known in the art for efficiently degreasing and/or cleaning the zinc or zinc alloy part.

Following such cleaning or pretreatment, the zinc part, e.g., zinc die casting, is rinsed with water, and the part is contacted, as by immersing same, in an aqueous electroless copper plating solution according to the invention.

Such novel electroless copper plating compositions or aqueous (watery) baths for plating copper on the zinc or zinc alloy part, e.g., zinc die casting, contains as one essential component a soluble copper salt. Examples of such copper salt which can be employed include copper sulfate, copper chloride, copper nitrate, copper acetate, copper cyanide, and the like.

A second essential component of the electroless copper plating composition or bath according to the invention is a complexing agent. Any suitable complexing agent for copper can be employed. Examples of such complexing agents include carboxylic acids such as acetic acid, propionic acid, citric acid, tartaric acid, and including amino substituted carboxylic acids such as aminoacetic acid and ethylenediamine tetraacetic acid, and also inorganic acids such as pyrophosphoric acid and boric acid, all of which acids can be present in the form of their soluble, e.g., alkali metal, salts, such as their sodium and potassium salts; amines, such as ethylene diamine, diethylene triamine, triethylene tetramine, ammonia, ammonium hydroxide, amine and ammonium salts of the above acids, such as the above noted amine and ammonium salts, of the above carboxylic acids, and soluble cyanide salts, e.g., the alkali metal salts such as the sodium salts, and the like.

Where copper cyanide is employed as the copper salt component, the anion, that is cyanide anion, in the form of the alkali metal salt, e.g., sodium cyanide can be employed as complexing agent. Also, a single compound or salt can furnish the copper cation, and also an anion such as the cyanide ion which functions as the complexing agent.

A third essential component of the electroless copper plating baths of the invention is a reducing agent. Suitable reducing agents for this purpose include, for example, hypophosphorus acid, and soluble salts thereof, usually in the form of the alkali metal salt, such as sodium hypophosphite, formaldehyde, thiosulfates, e.g., sodium or potassium thiosulfate, borohydrides, e.g., the sodium or potassium borohydrides, hydroxylamine, hydrazine, and the like.

As a preferred optional component, although not necessary, is the incorporation of a trace amount of a sulfur-bearing compound, such as thiourea, thiosulfate, dimethyl sulfoxide, and the like. It has been found that the incorporation of such small amount of a sulfur-bearing compound such as thiourea in the electroless copper plating bath effects more rapid plating of the electroless copper on the zinc or zinc alloy substrate treated with the electroless copper plating solution. Where thiosulfate is used as reducing agent, this compound can also function as sulfur-bearing compound for the above purpose.

The pH of the electroless copper plating bath of the invention can range from about 5.0 to about 13.0, and preferably is maintained in the range of about 5.0 to about 8.0. The pH of such bath can be adjusted upward by the addition of alkali, such as sodium hydroxide, especially where the complexing agent employed is an acid such as a carboxylic acid, e.g., citric acid, as noted above, or downward by the addition of acids, preferably carboxylic acids such as citric acid. The electroless copper plating baths are generally operated in the lower portion of the above noted pH range, that is the preferred 5.0 to about 8.0 pH range. In such lower pH ranges, it has been found that generally as complexing agents, the above noted carboxylic acid complexing agents work best, and the complexing agents also should be selected from those which do not readily attack zinc at these lower pH ranges.

Where cyanides are employed as complexing agents, no adjustment of the pH of the electroless plating solution is generally required, since these compounds, which are usually added as their alkali metal salts, often provide the solution with a pH ranging from about 9.0 to about 13. Solutions containing cyanides are maintained highly basic as a precaution against the evolution of poisonous HCN gas evolved on the acid side of the above pH range.

Where amines and ammonia are employed as complexing agents, the pH of the electroless plating solution can be adjusted to the desired value and maintained by the addition of a carboxylic acid as described above.

The proportions of the components of the electroless copper plating baths of the invention can vary. However, it has been found that the amount of the copper salt should range from about 0.5 to about 20 percent, preferably about 1 to about 5 percent, by weight of the solution. The amount of complexing agent employed should not be less than about one-half the amount of the copper salt present and not more than about 10 times the amount of the copper salt. In the low pH operating ranges, e.g., between pH about 5.0 to about 8.0, an amount of complexing agent preferably is employed ranging from about an equal amount with respect to the copper salt to about 5 times as much as the copper salt. In the high pH ranges of say from about 8.0 up to about 13.0, the amount of complexing agent employed preferably can range from about an equal proportion with respect to the copper salt, to about 10 times the amount of copper salt. Usually, it has been found that larger amounts of the complexing agents are more effective at the higher end of the pH range. An exception to this is that in those highly basic electroless copper solutions containing a cyanide as complexing

agent, the amount of such complexing agent employed is somewhat lower, ranging from an amount equal to the amount of copper salt to about 5 times the amount of such salt.

The amount of reducing agent employed in the electroless copper plating baths according to the invention can vary from about one-fourth of the amount of copper salt employed, up to about 3 times as much, an optimum amount being substantially the same amount as that of the copper salt present.

The amount of sulfur-bearing compound which can be employed in the electroless copper plating solution of the invention can range from 0 to about 50, e.g., about 0.1 to about 50, mg per liter. Where the electroless copper plating solution is employed in the lower portion of the pH range, e.g., between pH about 5.0 and about 8.0, the amount of sulfur-bearing compound, e.g., thiourea or thiosulfate, employed is maintained on the low side of the above range, e.g., from about 0.1 to about 10 mg per liter, and where so employed, it can be used effectively in an amount of about 0.5 mg per liter. However, as previously noted, the electroless copper plating solutions of the invention can be operated in the absence of a sulfur-bearing compound, while still obtaining highly improved results.

The temperature of treatment of the zinc or zinc alloy part in the above noted electroless copper plating solutions of the invention can range from as low as about 55°C up to about the boiling point of the solutions, e.g., up to about 100°C, and preferably is maintained between about 80° and about 95°C.

Time of treatment of the zinc or zinc alloy part in the electroless copper plating solutions of the invention can range from as little as about 10 minutes up to about 1 hour or more, depending in large measure upon the specific composition of the solution and the temperature thereof.

The zinc or zinc alloy part, e.g., zinc die casting, treated in the electroless copper plating solution of the invention, is removed from such bath and rinsed. A highly adherent uniform continuous copper coating is thus bonded to the zinc or zinc alloy substrate.

According to one mode of procedure, the zinc or zinc alloy part containing the electroless copper coating is then contacted, as by immersion of the part, in an aqueous electroplating bath, e.g., containing copper cyanide, known in the art as a copper cyanide strike.

The zinc or zinc alloy part containing a thin electroplated copper coating or copper strike over the initially applied electroless copper coating, is then rinsed, and treated or contacted as by immersion of the part, in a conventional bright aqueous acid copper electroplating bath, containing, e.g., copper sulfate, an acid, e.g., sulfuric acid and/or hydrochloric acid, and optionally, small amounts of conventional levelers and/or brighteners, such as aryl ring compounds, e.g., benzene or toluene, or acetylenic compounds, e.g., butynols, together with lead, arsenic or sulfur compounds, such levelers and brighteners tending to smooth and to brighten the electroplated copper surface. The result is the production of a second electroplated copper coating having a bright finish, over the underlying thin electroplated copper strike, and the initial electroless copper plating.

At this point, a highly adherent continuous bright copper plating is securely bonded to the zinc or zinc alloy substrate, via the underlying above noted electrolytic and electroless copper undercoats, with no pinholes therein, and without any poisoning of the copper electroplating baths, since the uniform coating of electroless copper initially applied completely covers the zinc or zinc alloy substrate leaving no bare zinc spots. The copper coated part, if desired, can then be treated further to protect the copper coating from discoloration and corrosion, by application of resins or plastics, e.g., acrylics, polyurethanes, polyethylene, polypropylene, polyamide (nylon), and the like, by plastic coating procedures known in the art.

However, in preferred practice for producing a bright chrome hard and corrosion resistant plating on the zinc or zinc alloy, e.g., zinc die casting, substrate, for many uses of such parts, e.g., as bathroom fixtures, as noted above, the bright copper coated zinc alloy part is treated or contacted as by immersion, in a conventional bright electroplating nickel bath, e.g., containing a nickel salt, such as nickel chloride or sulfate, which can also contain suitable levelers and brighteners of the types noted above. This operation forms a nickel overcoat on the bright copper coating, providing additional corrosion protection to that provided by the underlying copper coatings.

The nickel plated zinc or zinc alloy part is then treated or contacted as by immersion, in a conventional bright chrome aqueous electroplating bath, containing chromic acid, and which can also contain a small amount of sulfuric acid.

Following treatment of the zinc or zinc alloy part in the bright chrome electroplating bath, the result is a hard uniform continuous plating of corrosion resistant chrome over the electroplated nickel, electroplated bright copper and copper strike, and electroless copper undercoats. Such chrome plating provides high corrosion resistance for the zinc or zinc alloy substrate, and is a bright attractive coating, substantially free of pits, and any bare zinc spots.

The application of the electroless copper plating to the zinc or zinc alloy substrate, due to its complete coverage of the zinc or zinc alloy substrate without leaving any bare zinc spots, prevents poisoning not only of the subsequent copper electroplating baths, but of the subsequent nickel and chrome electroplating baths.

If desired, the above described sequence of operations can be altered, by first treating, as by immersion, the cleaned zinc or zinc alloy, e.g., zinc die casting, in the above noted copper cyanide electroplating bath (the cyanide strike), to produce a very thin copper electroplate or copper strike over the base substrate, followed by treatment of the resulting zinc or zinc alloy part having the thin copper strike, in the above described electroless copper plating solution of the invention to form electroless copper over the initial thin copper strike or electroplate, followed by the above described sequence of operations, including treatment in the bright copper electroplating bath followed, if desired, by application of resins or plastics to the bright copper electroplate, or alternatively, by treatment of the part containing the bright copper electroplate first in a nickel electroplating bath, followed by treatment in a chrome electroplating bath, as described above. Es-

essentially the same improved results and advantages are obtained by this procedure as by that described above wherein the zinc or zinc alloy part is initially treated in the electroless copper solution of the invention, followed by treatment in the copper cyanide strike solution.

In place of a copper cyanide strike solution, a copper pyrophosphate strike solution can be employed, if desired, in any of the above procedures to produce the thin copper strike on the zinc or zinc alloy part.

Alternatively, the above noted treatment in the copper cyanide or copper pyrophosphate strike solution can be entirely omitted, and the zinc or zinc alloy part, following cleaning thereof, can be treated initially in the electroless copper plating solution of the invention as described above, followed directly by treatment in the bright copper electroplating bath to form a copper electroplate over the electroless copper initial coating. The part can then be overcoated with a resin or plastic, or treated as noted above, in a nickel electroplating bath followed by treatment in a bright chrome electroplating bath. By this procedure, it was found that essentially the same improved results, namely, the formation of highly adherent and continuous copper, nickel and bright chrome electroplates, in the substantial absence of bare zinc spots, are achieved, clearly evidencing that treatment in the electroless copper plating bath according to the invention provides good copper plating coverage, in the absence of the use of the above copper strike electroplating baths. The latter is the preferred procedure.

The following are examples of practice of the invention, described in connection with the accompanying drawing, wherein

FIGS. 1 to 5 illustrate various modifications of a zinc die casting containing a metal plated system including an electroless copper plate or coating. The drawing is exaggerated for greater clarity.

#### EXAMPLE 1

A zinc die casting having the Composition (A) above is first degreased in 1,1,1-trichlorethane for a period of 15 minutes, and the degreased die casting is then subjected to anodic cleaning in the following aqueous solution:

| Components                | Grams/Liter |
|---------------------------|-------------|
| Tetrasodium pyrophosphate | 40          |
| Borax                     | 70          |
| Sodium fluoride           | 20          |

Anodic cleaning in the above solution is carried out at 75°C for 3 minutes at 3 volts.

Following rinsing in water, the zinc die casting is then dipped in the aqueous zincate solution noted below:

| Components       | Ounces/Gal. |
|------------------|-------------|
| Sodium Hydroxide | 14          |
| Zinc oxide       | 2.5         |

Treatment in the above zincate solution is carried out at ambient temperature for a period of about 3 minutes, and the die casting removed from the solution is then rinsed.

Following such cleaning of the zinc die casting, the part is dipped in an electroless copper bath, Composi-

tion 1 noted below, maintained at a temperature of 95°C, for 10 minutes.

| Composition 1                | Grams/Liter |
|------------------------------|-------------|
| Copper sulfate               | 20.0        |
| Sodium hypophosphite         | 20.0        |
| Citric acid                  | 40.0        |
| Thiourea                     | ¼ mg/l      |
| pH adjusted to 5.8 with NaOH |             |

The zinc die casting containing the electroless copper coating is then rinsed with water and dipped in a bright copper aqueous electroplating bath consisting essentially of the following composition:

| Components     | Ounces/Gal. |
|----------------|-------------|
| Copper sulfate | 26.5        |
| Sulfuric acid  | 4.0         |

Copper electroplating is carried out in the above bath at 65 amperes/ft<sup>2</sup>, with the time of plating being 5 minutes.

The zinc die casting containing a bright copper plate over the electroless copper plate, is rinsed with water and is then dipped in a bright nickel aqueous electroplating solution consisting essentially of the following composition:

| Components      | Ounces/Gal. |
|-----------------|-------------|
| Nickel sulfate  | 44          |
| Nickel chloride | 6           |
| Boric acid      | 5           |

The pH of the above bath is 3.0, the temperature of the bath is maintained at 130°F, and the nickel electroplating is carried out at a current density of 50 amperes/ft<sup>2</sup> for a period of time of 5 minutes.

The zinc die casting now containing an electroless copper plate, a bright copper electroplate and a bright nickel electroplate is rinsed with water and dipped in a bright chrome aqueous electroplating bath of the following composition:

| Components    | Ounces/Gal. |
|---------------|-------------|
| Chromic acid  | 33.0        |
| Sulfuric acid | 0.33        |

The above chromic acid electroplating bath is maintained at a temperature of 110°F and is operated at a current density of 200 amperes/ft<sup>2</sup>, the die casting being treated for a period of 2 minutes in this bath.

The zinc die casting removed from the chromic acid electroplating bath is rinsed with water. Referring to the drawing, the zinc die casting indicated at 10 now has a hard bright uniform continuous chrome plate 18 with underlying coatings of electroplated nickel 16, electroplated copper 14, and electroless copper 12. The chrome plating 18 is observed to be free of pits and of any bare zinc spots, and has high corrosion resistance.

It is observed that the bright copper plating bath, bright nickel plating bath and the bright chrome plating bath all remain effective over long periods of treatment of zinc die castings according to the above procedure of this example, without any significant amounts of zinc being dissolved in such baths, and accordingly without zinc poisoning of such baths, indicating that the electroless copper plating 12 initially applied over the zinc

die casting 10 forms a continuous plating with no pin-holes or bare zinc spots.

#### EXAMPLE 2

The procedure of Example 1 is repeated, except that after cleaning of the zinc die casting in the anodic cleaner, and prior to treatment in the electroless copper bath, the cleaned zinc die casting is dipped in an aqueous copper cyanide strike solution having the following composition:

| Components     | Ounces/Gal. |
|----------------|-------------|
| Copper cyanide | 3           |
| Sodium cyanide | 5           |

The temperature of the above copper cyanide aqueous solution is maintained at 130°F, the bath is operated at 5 volts and the zinc die casting is treated for 1 ½ minutes in this bath.

The zinc die casting removed from the bath contains a thin electroplated copper coating or copper strike, and is rinsed with water, and then treated consecutively in the electroless copper plating bath, the bright copper electroplating bath, the bright nickel electroplating bath, and finally in the bright chrome electroplating bath, as described in Example 1.

Substantially the same results are achieved here as in Example 1 above, referring to FIG. 2 of the drawing, in the form of a zinc die casting 10 having a hard, corrosion resistant bright pitless chrome plating 18 free of bare zinc spots, over undercoats including first the copper strike 11, the electroless copper coating 12, the bright copper electroplate 14, and finally the bright nickel electroplate 16, over which is disposed the bright chrome plating 18.

#### EXAMPLE 3

The procedure of Example 2 is followed, except that treatment of the zinc die casting in the copper cyanide strike solution is carried out following treatment in the electroless copper bath and prior to treatment in the bright copper electroplating bath.

Results substantially the same as in Example 2 are obtained, referring to FIG. 3 of the drawing, the zinc die casting 10 having a bright hard uniform corrosion resistant chrome plate 18 free of pits and bare zinc spots, over a series of undercoatings including first an electroless copper plate 12 followed by a copper strike 11, a bright copper electroplate 14, and a bright nickel electroplate 16, with the bright chrome plate 18 thereover.

#### EXAMPLE 4

The procedure of Example 1 is repeated through treatment of the zinc die casting in the bright copper electroplating solution, followed by rinsing.

The zinc die casting containing a bright copper electroplate over the electroless copper coating, is then treated with a clear resin to form a plastic coating over the bright copper electroplate. This is carried out by applying as by dipping the zinc die casting in a solvent solution, e.g., a methyl ethyl ketone solvent solution, of an acrylic resin, followed by drying to remove the solvent and forming the resin coating.

Referring to FIG. 4 of the drawing, the resulting zinc die casting 10 has a clear continuous acrylic resin coating 20 over the bright copper electroplate 14 in turn covering the electroless copper undercoat 12.

#### EXAMPLE 5

The procedure of Example 1 is repeated except that in the cleaning sequence for the zinc die casting, in place of the use of anodic cleaning, the degreased die casting is dipped in an aqueous alkaline solution containing 5 percent trisodium phosphate, 5 percent sodium hydroxide and 0.25 percent Igepal C.O. 630, understood to be a surfactant in the form of an alkylphenoxypoly (ethyleneoxy) ethanol, at 90°C. for 15 minutes, and then rinsed with water, following which the zinc die casting is treated with the alkaline zincate solution, rinsed and then treated in a 5 percent citric acid dip at ambient temperature for 3 minutes. After rinsing, the cleaned zinc die casting is then subjected to the sequence of plating operations set forth in Example 1, including electroless copper plating, bright copper electroplating, bright nickel electroplating, and bright chrome electroplating.

Results similar to those set forth in Example 1 are obtained.

#### EXAMPLE 6

The procedures of Examples 1 to 5 are repeated employing substantially pure zinc in place of the zinc die casting.

Results comparable to the results of Examples 1 to 5 are obtained.

#### EXAMPLE 7

The procedure of Examples 2 and 3 are repeated except that in place of the copper cyanide strike solution employed therein, an aqueous copper pyrophosphate strike solution is utilized having the following composition:

| Components              | Ounces/Gal. |
|-------------------------|-------------|
| Copper pyrophosphate    | 4           |
| Potassium pyrophosphate | 26          |

The pH of the above copper pyrophosphate solution is 8.5 and is operated at a temperature of 130°F with agitation at a current density of 5 amperes/ft<sup>2</sup>, the zinc die casting being contacted with such solution for 3 minutes.

Substantially the same results are obtained as in Examples 2 and 3.

#### EXAMPLE 8

The procedures of Examples 1, 2 and 3 are followed, in each case employing the respective electroless copper aqueous solutions set forth in the table below, under the listed conditions of pH, temperature and time of treatment set forth in the table.

TABLE.—ELECTROLESS COPPER PLATING AQUEOUS BATHS FOR ZINC OR ZINC ALLOYS

|                                   | Compositions (grams/liter) |     |     |     |     |     |     |     |     |     |     |      |     |    |    |     |     |     |    |    |    |    |    |    |  |
|-----------------------------------|----------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|-----|----|----|-----|-----|-----|----|----|----|----|----|----|--|
| Components                        | 2                          | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  | 13   | 14  | 15 | 16 | 17  | 18  | 19  | 20 | 21 | 22 | 23 | 24 | 25 |  |
| Copper sulfate                    |                            | 10  | 30  | 30  | 20  | 20  | 20  | 20  | 20  | 20  | 20  | 20   | 20  | 20 |    | 20  | 20  | 20  | 20 | 30 |    |    |    |    |  |
| Copper chloride                   | 20                         |     |     |     |     |     |     |     |     |     |     |      |     |    |    |     |     |     |    |    |    | 10 |    | 20 |  |
| Copper cyanide                    |                            |     |     |     |     |     |     |     |     |     |     |      |     |    | 20 |     |     |     |    |    |    |    | 10 |    |  |
| Copper acetate                    |                            |     |     |     |     |     |     |     |     |     |     |      |     |    |    |     |     |     |    |    | 40 |    |    |    |  |
| Citric acid                       | 40                         | 20  | 60  | 60  | 20  | 40  |     |     | 40  | 40  | 40  | 40   |     |    |    |     |     |     |    |    |    |    |    |    |  |
| Tartaric acid                     |                            |     |     |     |     |     | 40  |     |     |     |     |      |     |    |    |     |     |     |    |    |    |    |    | 60 |  |
| Propionic acid                    |                            |     |     |     |     |     |     | 40  |     |     |     |      |     |    |    |     |     |     |    |    |    |    |    |    |  |
| Tetrasodium pyrophosphate         |                            |     |     |     |     |     |     |     |     |     |     |      | 80  | 40 |    |     |     |     |    |    |    |    | 30 |    |  |
| Sodium cyanide                    |                            |     |     |     |     |     |     |     |     |     |     |      |     | 30 |    |     |     |     |    |    |    |    |    |    |  |
| Ethylene diamine                  |                            |     |     |     |     |     |     |     |     |     |     |      |     |    |    |     | 20  |     |    |    |    |    |    |    |  |
| Diethylene triamine               |                            |     |     |     |     |     |     |     |     |     |     |      |     |    |    |     |     | 20  |    |    |    |    |    |    |  |
| Boric acid                        |                            |     |     |     |     |     |     |     |     |     |     |      |     |    |    |     |     |     | 30 |    |    |    |    |    |  |
| Ammonium citrate                  |                            |     |     |     |     |     |     |     |     |     |     |      |     |    |    | 60  |     |     |    |    |    |    |    |    |  |
| Ethylene diamine tetraacetic acid |                            |     |     |     |     |     |     |     |     |     |     |      |     |    |    |     |     |     |    | 50 |    | 60 |    |    |  |
| Sodium hypophosphite              | 20                         | 10  | 30  | 15  | 20  | 20  | 20  | 20  | 20  | 20  | 20  | 20   | 20  | 20 | 20 | 20  | 20  | 20  | 20 |    |    |    |    |    |  |
| Sodium thiosulfate                |                            |     |     |     |     |     |     |     |     |     |     |      |     |    |    |     |     |     |    | 25 |    |    |    | 10 |  |
| Sodium borohydride                |                            |     |     |     |     |     |     |     |     |     |     |      |     |    |    |     |     |     |    |    | 40 | 25 | 20 |    |  |
| Thiourea (mg./liter)              | 0.5                        | 0.5 | 0.5 | 0.5 | 0.5 |     | 0.5 | 0.5 | 1.0 | 4.0 | 0.5 | 0.5  | 0.5 |    |    |     | 0.5 | 0.5 |    |    |    |    |    |    |  |
| Dimethyl sulfoxide (mg./liter)    |                            |     |     |     |     |     |     |     |     |     |     |      |     |    |    |     |     |     |    |    | 5  |    |    | 20 |  |
| Sodium thiosulfate (mg./liter)    |                            |     |     |     |     |     |     |     |     |     |     |      |     |    |    |     |     |     |    |    | 10 |    |    |    |  |
| Bath, pH                          | 5.8                        | 5.8 | 5.8 | 5.8 | 5.8 | 5.8 | 5.8 | 5.8 | 5.8 | 8.0 | 5.8 | 11.5 |     |    |    | 5.8 |     |     |    |    |    |    |    |    |  |
| Temperature, ° C.                 | 95                         | 95  | 95  | 95  | 95  | 80  | 95  | 95  | 95  | 95  | 95  | 95   | 95  | 95 | 70 | 95  | 95  | 95  | 95 | 65 |    |    |    |    |  |
| Time of treatment (min.)          | 10                         | 30  | 10  | 20  | 20  | 15  | 15  | 15  | 15  | 15  | 15  | 15   | 15  | 15 | 15 | 15  | 15  | 15  | 15 | 15 |    |    |    |    |  |

Using the respective electroless copper baths of the table above, in each of Examples 1, 2 and 3, substantially the same improved results are obtained, in the form of a zinc die casting having a hard, bright, uniform continuous corrosion resistant chrome plating over the various metal undercoats set forth in each of Examples 1, 2 and 3 above, and illustrated in FIGS. 1 to 3 of the drawing.

#### EXAMPLE 9

The following are additional examples of electroless copper baths according to the invention:

| Components           | Composition (Grams/Liter) |      |
|----------------------|---------------------------|------|
|                      | 26                        | 27   |
| Copper sulfate       | 20                        | 20   |
| Sodium hypophosphite | 20                        | 20   |
| Acetic acid          | 40                        |      |
| Aminoacetic acid     |                           | 30   |
| pH                   | 8.0                       | 5.8  |
| or                   | 5.8                       | 10.5 |

Temperature of treatment in the above solutions is 95°C, for a period of 15 minutes, the pH of the above solutions being adjusted as noted above by addition of sodium hydroxide or citric acid.

Although in the description above and in preferred practice, a copper electroplate in the form of a bright copper electroplate is applied directly over the electroless copper coating on the zinc or zinc alloy part, it will be understood that other metal electroplates can be applied directly over the electroless copper coating, such as a bright nickel plate, over which can be applied a bright chrome electroplate. The following is an example of the latter embodiment.

#### EXAMPLE 10

The procedure of Example 1 is followed through treatment of the zinc die casting in the electroless copper solution, followed by rinsing.

Thereafter the zinc die casting containing the electroless copper plate is treated first in the bright nickel electroplating bath and then in the bright chrome electroplating bath, as described in Example 1.

The resulting zinc die casting, referring to FIG. 5 of

the drawing, now has a hard bright continuous chrome plate 18 with underlying coatings of electroplated nickel 16 and electroless copper 12. The chrome plating is uniform, free of pits and zinc bare spots, and has good corrosion resistance. However, the overall plating system of this example does not have the superior toughness and corrosion resistance of the plating system for the zinc die casting described in Example 1 including an intermediate copper electroplate between the electroless copper coating and the nickel electroplate.

From the foregoing, it is seen that the invention provides improved procedure for copper plating zinc or its alloys, particularly zinc die casting, employing a novel electroless copper plating operation, the resulting copper electroless coating providing a base for application of electroplated copper and other metals such as nickel and chrome plating, or for application of a plastic coating, for production of bright highly attractive coatings or metal plates on zinc or zinc alloy parts, having high corrosion resistance and high uniformity and surface coverage, without formation of pits or pinholes in the respective metal platings or coatings and in the absence of zinc bare spots, thus also avoiding zinc poisoning of the various electroplating baths.

While I have described particular embodiments of the invention for purposes of illustration, it will be understood that various changes and modifications can be made therein within the spirit of the invention, and the invention accordingly is not to be taken as limited except by the scope of the appended claims.

I claim:

1. In the process of producing a uniform continuous bonded copper coating on a metal body selected from the group consisting of zinc and its alloys, the improvement which comprises contacting said metal body with an aqueous electroless copper plating solution consisting essentially of a soluble copper salt, a complexing agent, and a reducing agent, to form an electroless copper coating on said metal body, prior to electrodepositing a coating on said metal body in a subsequent metal electroplating bath.

2. The process as defined in claim 1, said copper salt being selected from the group consisting of copper sulfate, copper chloride, copper nitrate, copper acetate and copper cyanide; said complexing agent being selected from the group consisting of carboxylic acids,

pyrophosphoric acid, boric acid, and the alkali metal salts of said acids, ammonia, ammonium hydroxide, amines, amine and ammonium salts of said acids, and soluble cyanides; and said reducing agent being selected from the group consisting of hypophosphorus acid and soluble salts thereof, formaldehyde, thiosulfates, borohydrides, hydroxylamine and hydrazine; the pH of said solution ranging from about 5.0 to about 13.0, and the temperature of said electroless copper plating solution being maintained between about 55°C and about boiling.

3. The process as defined in claim 2, said complexing agent being citric acid, and said reducing agent being an alkali metal hypophosphite, the pH of said solution ranging from about 5.0 to about 8.0, and said temperature ranging from about 55°C to about 100°C.

4. The process as defined in claim 3, said copper salt being copper sulfate and said temperature ranging from about 80 to about 95°C.

5. The process as defined in claim 4, the amount of said copper salt present ranging from about 1 to about 5 percent, by weight of the electroless copper plating solution, the amount of said complexing agent employed ranging from about one-half the amount of the copper salt to about 10 times the amount of said copper salt, and the amount of said reducing agent employed ranging from about one-fourth of the amount of the copper salt employed to about 3 times the amount of said copper salt present, said solution being adjusted to a pH of about 5.8 by the addition of sodium hydroxide, the temperature of treatment in said solution ranging from about 80 to about 95°C, said metal body being contacted in said electroless copper plating solution for a period ranging from about 10 minutes up to about 1 hour.

6. The process as defined in claim 5, and after treatment of said metal body in said electroless copper plating solution, contacting said metal body containing said electroless copper coating with an aqueous acid copper electroplating bath containing a soluble copper salt, and forming a copper electroplate coating over said electroless copper coating, including additionally contacting said metal body containing said electroless copper and copper electroplate coatings, with a nickel electroplating solution containing a nickel salt, and depositing a nickel electroplate on said copper electroplate coating, and then contacting said metal body with an aqueous chromic acid electroplating solution, and depositing a chrome electroplate over said nickel electroplate.

7. The process as defined in claim 4, wherein the electroless copper plating solution additionally contains thiourea.

8. The process as defined in claim 3, and after treatment of said metal body in said electroless copper plating solution, contacting said metal body containing said electroless copper coating with an aqueous acid copper electroplating bath containing a soluble copper salt, and forming a copper electroplate coating over said electroless copper coating, including additionally contacting said metal body containing said electroless copper and copper electroplate coatings, with a nickel electroplating solution containing a nickel salt, and

depositing a nickel electroplate on said copper electroplate coating, and then contacting said metal body with an aqueous chromic acid electroplating solution, and depositing a chrome electroplate over said nickel electroplate.

9. The process as defined in claim 3, and after treatment of said metal body in said electroless copper plating solution, contacting said metal body containing said electroless copper coating with an aqueous acid copper electroplating bath containing a soluble copper salt, and forming a copper electroplate coating over said electroless copper coating.

10. The process as defined in claim 2, wherein the electroless copper plating solution additionally contains up to 50 mg per liter of a sulfur-bearing compound selected from the group consisting of thiourea, thiosulfate and dimethyl sulfoxide.

11. The process as defined in claim 1, and after treatment of said metal body in said electroless copper plating solution, contacting said metal body containing said electroless copper coating with an aqueous acid copper electroplating bath containing a soluble copper salt, and forming a copper electroplate coating over said electroless copper coating.

12. The process as defined in claim 11, including additionally contacting said metal body containing said electroless copper and copper electroplate coatings, with a nickel electroplating solution containing a nickel salt, and depositing a nickel electroplate on said copper electroplate coating, and then contacting said metal body with an aqueous chromic acid electroplating solution, and depositing a chrome electroplate over said nickel electroplate.

13. The process as defined in claim 1, the amount of said copper salt present ranging from about 1 to about 5 percent, by weight of the electroless copper plating solution, the amount of said complexing agent employed ranging from about one-half the amount of the copper salt to about 10 times the amount of said copper salt, and the amount of said reducing agent employed ranging from about one-fourth of the amount of the copper salt employed to about 3 times the amount of said copper salt present.

14. The process as defined in claim 1, including contacting said metal body with a degreaser, and then contacting said metal body with an alkaline cleaner, to remove surface dirt and soils from said metal body, prior to contacting same with said electroless copper plating solution.

15. The process as defined in claim 1, and after treatment of said metal body in said electroless copper plating solution, contacting said metal body containing said electroless copper coating with a metal electroplating bath, and forming a metal electroplate coating over said electroless copper coating.

16. The process as defined in claim 1, including subjecting said metal body to anodic cleaning in an alkaline solution containing a soluble fluoride, followed by treatment of said metal body in an aqueous zincate solution, prior to contacting said metal body with said electroless copper plating solution.

17. The process as defined in claim 1, the amount of said copper salt present ranging from about 0.5 to about 20 percent, by weight of the electroless copper plating solution.

\* \* \* \* \*