This invention relates to improvements in the art of electroplating copper or copper alloys on a zinc or zinc alloy surface. The general object of the invention is to produce an article in which the overlying copper or copper alloy plate or deposit is free of "blisters."

The term "blistering" as used herein refers to that tendency of the copper or copper alloy plate to lift or peel away from a zinc surface. Blistering has been most evident and troublesome when the copper plated zinc article has had to be subjected to a subsequent heat treatment, as when the plated article was coated with a thermosetting resin or lacquer which then required baking at elevated temperatures for an extended period of time. Blistering frequently has occurred, however, during the copper plating operation itself, or when the plated article was simply allowed to age without being subjected to a heat treatment.

The prior procedures for plating copper or brass upon zinc die castings in an effort to produce a blister-free copper or brass plate, have not been successful. The selection of a zinc base die casting alloy conforming with ASTM Standard Specifications B86-43 and B186-42T, coupled with the best cleaning and plating practices, have been ineffective to consistently prevent the occurrence of blisters in the copper or brass plate, particularly when the plated article was subjected to heat.

We have determined that the presence of lead and/or cadmium at the interface of the zinc alloy die casting and the overlying copper or brass deposit is responsible for the formation of blisters. ASTM StandardSpecifications B86-43 and B186-42T specify that the compositions of the alloy shall contain not more than 0.007% lead and 0.005% cadmium. Nevertheless, even these seemingly minute quantities of lead and cadmium in the zinc alloy have the detrimental effect of causing blisters to form in the copper or brass plate overlying the zinc die casting. It appears that this detrimental effect is enhanced because the lead and/or cadmium tend to concentrate at the surface or in the skin of the die casting.

We have found that the tendency of the overlying copper or brass deposit to blister is reduced materially by interposing a layer or deposit of zinc which has a lead and cadmium content which is substantially less than the amount of lead and cadmium present in the skin of the zinc die casting. The best results are obtained by plating the zinc alloy die casting from a zinc solution which has been purified so that the resulting zinc plate is substantially free of lead and cadmium.

Our tests have shown that a zinc die casting made from an alloy conforming with ASTM Standard Specifications referred to above, when plated from a zinc plating solution containing approximately 0.0002 ounce of lead and cadmium per gallon of plating solution prior to the copper or brass plating, results in an article wherein the copper or brass plate will not blister though it be subjected to a temperature of 350° F. for a period of eighteen hours.

To prepare the lead and/or cadmium purified zinc plating solution, zinc dust is added to a conventional zinc plating solution. Such conventional plating solution may comprise ten (10) ounces per gallon of zinc cyanide, eight (8) ounces per gallon of sodium cyanide, and twelve (12) ounces per gallon of sodium hydroxide. The amount of zinc dust used is approximately two (2) pounds for each one hundred (100) gallons of solution. The zinc dust is kept in suspension by agitation. After approximately six (6) hours, agitation is discontinued and the zinc dust permitted to settle for a period of approximately twelve (12) hours. The solution then is filtered. This procedure results in the elimination of most of the lead and cadmium impurities.

To further purify the solution a current of low cathode current density may be passed through the solution and scrap material plated, using anodes which preferably contain less than 0.003% of lead and/or cadmium. The zinc plating solution thus prepared contains approximately 0.0002 ounce of lead and/or cadmium per gallon of solution.

The zinc alloy die casting to be plated is cleaned in a mild alkaline cleaning solution and rinsed. The die casting then is zinc plated from the substantially lead and cadmium free zinc solution heretofore described until a substantially continuous zinc deposit is obtained. Conventional zinc plating procedures are followed, using zinc anodes which preferably contain less than 0.003% of lead and/or cadmium. The zinc die casting thus zinc plated, then is plated with copper or brass from a conventional copper or brass plating solution in accordance with common practice in the art. In our work we have subjected the resultant articles to a temperature of 550° F. for a period of eighteen (18) hours, and no blisters developed in the copper or brass plate.

While the use of zinc dust to reduce the
amount of lead and cadmium in the zinc plating solution is preferred, it is within the scope of the invention to prepare a substantially lead and cadmium free zinc plating solution by any other suitable or known method. Sodium sulfide may be used to precipitate most of the lead and cadmium as lead and cadmium sulfides. The amount of lead and cadmium in the solution may be further reduced by plating on "dummies." While the best results for all conditions are obtained with an intermediate zinc deposit which is entirely or substantially free of lead and cadmium, if the copper plated article will not encounter heat in further processing or use, the time and effort required to obtain a zinc plating solution of such high degree of purity need not be expended. Where the copper or copper alloy plated die casting will not be subjected to a heat treatment in further processing or in use, it has been found adequate, to avoid blistering, to purify the zinc plating solution so that it contains not more than 0.0025 ounce of lead and/or cadmium per gallon of plating solution. Best commercial grades of zinc alloys for die castings contain a greater amount of lead and/or cadmium in the skin of an article cast from such alloys than the amount of lead and/or cadmium which is present in the deposit plate from a solution containing approximately 0.0025 ounce of lead and/or cadmium per gallon of solution in a bath having zinc anodes which preferably contain less than 0.005% of lead and/or cadmium. Continued plating from such solution will result in a further reduction in the amounts of lead and cadmium in the solution. Copper, tin and iron compounds may be present in an amount totalling 0.2 ounce per gallon of plating solution and will not interfere with the attainment of a non-blistering copper or copper alloy coating upon the zinc alloy die casting. While the lead and/or cadmium purified electrolyte has been described as a cyanide solution, it is within the scope of the invention to use any suitable zinc plating solution such as an acid zinc sulfate solution, or a zinc fluoroborate solution. The zinc cyanide solution, however, is preferred because of the simplicity of the procedure for removing or reducing the lead and cadmium therefrom. While the invention furnishes superior results in the plating of zinc alloy die castings with copper, brass or other copper containing alloys, excellent results also have been obtained in the plating of a metal base, other than a zinc alloy, where, in addition, it is desired to impart corrosion resistance to the underlying base metal. Ferrous metals such as steel, iron or any other suitable base metal may be zinc plated in a zinc solution from which the lead and cadmium has been substantially eliminated or reduced in the manner hereinbefore described, prior to plating with copper or any other deposit containing a substantial amount of copper. The zinc solution may have the lead and cadmium removed substantially entirely, or may contain as much as approximately 0.0025 ounce per gallon of the solution when the plating need not be relatively heat-resistant. While the surface deposits have been specifically described as copper and brass, it is within the scope of the invention to plate bronze or any other suitable deposit containing a substantial amount of copper upon the substantially lead and cadmium free zinc deposit. The term "deposit containing a substantial amount of copper," as used in the claims, refers to copper, as well as those alloys which contain a substantial amount of copper which are capable of being electrodeposited.

The term "zinc alloy base" as used in the claims is defined as a zinc alloy containing lead and cadmium in amounts present in commercially available alloys, or alloys conforms to ASTM Standards B36-49 and B186-497. It is believed that the method of our invention, as well as the advantages of the method and resultant articles produced thereby, will be apparent from the foregoing detailed description thereof. It will also be apparent that various changes may be made therein without departing from the spirit of the invention, as sought to be defined in the following claims.

We claim:

1. A method for providing a non-blistering deposit containing a substantial amount of copper upon a metal base selected from the group consisting of a ferrous base and a zinc alloy base, said method comprising plating zinc upon the metal base from a zinc solution containing not more than approximately 0.0025 ounce of lead and cadmium per gallon of solution, and plating a deposit containing a substantial amount of copper upon the zinc deposit.

2. A method for providing a non-blistering deposit containing a substantial amount of copper upon a zinc alloy base, said method comprising plating zinc upon the zinc alloy base from a zinc solution containing not more than approximately 0.0025 ounce of lead and cadmium per gallon of solution, and plating a deposit containing a substantial amount of copper upon the zinc deposit.

3. A method for providing a non-blistering deposit containing a substantial amount of copper upon a metal base selected from the group consisting of a ferrous base and a zinc alloy base, said method comprising plating zinc upon the ferrous base from a zinc solution containing not more than approximately 0.0025 ounce of lead and cadmium per gallon of solution, and plating a deposit containing a substantial amount of copper upon the zinc deposit.

4. A method for providing a relatively heat-resistant non-blistering deposit containing a substantial amount of copper upon a metal base selected from the group consisting of a ferrous base and a zinc alloy base, said method comprising plating zinc upon the metal base from a zinc solution containing not more than approximately 0.0025 ounce of lead and cadmium per gallon of solution, and plating a deposit containing a substantial amount of copper upon the zinc deposit.

5. A method for providing a relatively heat-resistant non-blistering deposit containing a substantial amount of copper upon a zinc alloy base, said method comprising plating zinc upon the zinc alloy base from a zinc solution containing not more than approximately 0.0025 ounce of lead and cadmium per gallon of solution, and plating a deposit containing a substantial amount of copper upon the zinc deposit.

6. A method for providing a relatively heat-resistant non-blistering deposit containing a substantial amount of copper upon a corrosion resistant ferrous base, said method comprising plating zinc upon the ferrous base from a zinc solution containing not more than approximately 0.0025 ounce of lead and cadmium per gallon of solution, and plating a deposit containing a substantial amount of copper upon the zinc deposit.

7. The method as defined in claim 4, wherein the deposit containing a substantial amount of copper.
copper is selected from the class consisting of copper, brass and bronze.

8. The method as defined in claim 5, in which the deposit containing a substantial amount of copper is selected from the class consisting of copper, brass and bronze.

9. The method as defined in claim 6, wherein the deposit containing a substantial amount of copper is selected from the class consisting of copper, brass and bronze.

HANS BERMAN.
SIGMUND KATZ.

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