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ZINC-COPPER-TIN ALLOY PLATING

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The present invention relates to a plating method for depositing, upon a platable cathode, a coating of high density, capable of taking a high polish, and highly resistant to corrosion and abrasion, such coating comprising an alloy consisting of zinc, copper and tin in suitable proportions. The invention relates, also to an electrolyte essential to the practice of the above method.

The primary object of the invention is to provide a method, and an electrolyte for use therein, whereby through the use of an anode composed of a suitable alloy of zinc, copper and tin, such alloy may be electro-deposited upon a suitable cathode, in substantially the proportions in which the ingredients appear in the anode. A further object of the invention is to provide and maintain, during the plating process, an electrolytic bath of such character as to support the electro-deposition of such alloy upon the cathode.

Still further objects of the invention will appear as the description proceeds.

To the accomplishment of the above and related objects, my invention may be embodied in the forms, and in the steps, described in the following specification, attention being called to the fact, however, that the specific embodiments described are by way of illustration only and that changes may be made therein so long as the scope of the appended claims is not violated.

I have discovered that an alloy, consisting of zinc approximately 90%, copper approximately 8.5% and tin approximately 1.5% has many highly desirable physical characteristics. Such an alloy has a density of approximately 7.24, a color, when unpolished, closely similar to that of cast aluminum, is capable of taking a high polish, has a ductility comparable to that of conventional copper or tin plate, is highly resistant to corrosion by substances encountered in nature, such as sea water and the like, resists ordinary abrasion, is weldable by ordinary methods, and is compatible with commercial types of solders and brazing metals. Additionally, I have found that, under suitable procedures, the alloy may be electro-deposited, substantially without change of proportion among its ingredients, at high efficiencies. When so deposited, under proper conditions, the plate retains the above characteristics and, when the plating process is properly controlled, the deposit will be found to possess a high metallic luster, without polishing or buffing, or with a minimum thereof.

I have found that a bath or electrolyte com-

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prising an aqueous solution of suitable proportions of suitable salts of the three metals embodied in this alloy, together with a suitable proportion of free cyanide, and preferably including also a substantial amount of a caustic alkali, is essential to the practice of my method. Preferably the zinc and copper will be introduced into the bath in the form of metal cyanides, while the tin is preferably introduced in the form of potassium stannate.

Experimentation has established the fact that the rate of corrosion of the metals from the anode may be to a considerable degree individually controlled by variations in the relative proportions in which free cyanide and caustic alkali are present in the electrolyte. Broadly speaking, an increase in the ratio of cyanide radical to caustic alkali in the electrolyte will result in an increase in the rate of corrosion of zinc and copper from the anode; while a decrease in that ratio will result in an increase in the rate of corrosion of tin from the anode. Conveniently, the free cyanide may be introduced into the bath as sodium cyanide, though any of the alkali cyanides may be used; while sodium hydroxide will preferably be used as the caustic alkali.

An optimum electrolyte may be prepared by dissolving, in one gallon of water,

	Ounces
NaOH	9
NaCN	13
$Zn(CN)_2$	8.75
CuCN	1
$K_2SnO_3 \cdot 3H_2O$	0.15

While the above proportions are optimum, according to my present belief, variations in the proportions of the ingredients, within the following ranges are permissible without substantial effect upon the functioning of the electrolyte or upon the end product.

	Ounces
NaOH	6.5–9
NaCN	3–13.5
$Zn(CN)_2$	6.5–11
CuCN	0.5–2
$K_2SnO_3 \cdot 3H_2O$	0.1–0.3

After the bath has been prepared, the cathode piece or pieces should be thoroughly cleaned, preferably in alkaline electrolytic cleaner such as a 4% good commercial cleaner compound at a boiling temperature. If steel parts are to be plated, it is preferable to subject them to a re-

verse current for a short period; and, of course, a degreasing solution should be used if the condition of the parts to be plated so indicates. The parts should then be rinsed thoroughly, dipped in a 20% commercial muriatic or sulfuric acid, and then again thoroughly rinsed in cold water.

Now, the cathode pieces may be suitably suspended in the electrolytic bath above described, preferably arranging the cathode parts in pairs equally and oppositely spaced from the anodes similarly suspended in the bath. Each anode will preferably present a flat face toward each of the pair of cathodes associated therewith, the cathodes being preferably spaced approximately five inches from such faces. Each anode may be a cast bar of the alloy above defined, comprising approximately 90% zinc, 8.5% copper and 1.5% tin. A plating current of 25 to 45 amperes per square foot, at a potential of 3 to 4 volts, is now applied between the anode and the cathodes, a density of 30 to 37.5 amperes per square foot, depending upon cathode shape, being optimum. I have found that the potential will sometimes rise above 4 volts in the early stages of the process; but that, after a few minutes, it will drop to a value of 3½ to 4 volts where it will continue quite steadily throughout the plating operation. Under such conditions, a deposit of 0.0001 inch thickness will be formed upon the cathode every 3½ to 4 minutes; and I believe this deposit rate to be optimum. My best results have been attained through the use of a potential of 3.8 volts at a density of 35 amperes per square foot of cathode surface.

The temperature of the bath should preferably be held between 80° and 90° F.; though my experiments indicate that the process will not be substantially affected if the temperature is permitted to drop as low as 70° or to rise as high as 140°.

After the desired thickness of deposit has been formed on the cathodes, they should be removed from the bath, rinsed in boiling water and then suitably dried. It will be found that a bright, white deposit, closely resembling a good cadmium plate in appearance and physical characteristics, will have been formed.

The platable metal content of the bath (zinc, copper and tin) should preferably be present substantially in the proportions in which those metals appear in the anode; viz., zinc 90%, copper 8.5% and tin 1.5%. It will be seen that the bath, as originally prepared in accordance with the above instructions, contains zinc 86.35%, copper 12.59% and tin 1.06%. When the plating current is applied between the defined anode and a suitable cathode for a period of, for instance, twelve hours, it is found that the composition of the bath, as concerns the platable metals, will have been changed to contain zinc 5.51 ounces, or 90.33%, copper 0.50 ounces, or 8.20% and tin 0.09 ounces or 1.47%, per gallon of solution. This is a result, of course, of differing rates of corrosion of the respective metals from the anode into the solution, as related to the rates of deposition of the respective metals upon the cathode.

It will be noted that, in the bath as originally prepared, the cyanide radical, obtained as sodium cyanide, is present in the amount of 20.85 ounces per gallon, while platable metals are present to the amount of 5.64 ounces per gallon. Thus, as originally prepared, the ratio of cyanide, obtained as sodium cyanide, to total platable metals is 3.70. After twelve hours of plating, however, it will be found that total cyanide in the bath, obtained as sodium cyanide, will be 12.7 ounces per gallon; so that the ratio of cyanide, obtained as sodium cyanide, to total platable metals, will now be 2.08.

I presently believe that control of the ratio of total cyanide to total platable metals, in the bath, within a range from 1.90 to 3.75 is desirable in order to produce optimum results; and that a ratio close to 2.50 should be maintained during continuous plating operation. Thus, to the bath of the composition above described after twelve hours of operation, I prefer to add 2.55 ounces of sodium cyanide per gallon of electrolyte, or an equivalent mass of some other alkali cyanide.

If the cyanide-to-metals ratio rises substantially above 2.5, during operation, the ratio may be restored to approximately the optimum value by the addition of sodium hydroxide, or some other caustic alkali, in quantities sufficient to increase the rate at which the anode metals will be attacked and corroded or dissolved in the electrolyte.

Under conditions as above described, the efficiency of the present plating method is unusually high. For instance, during a twelve-hour test under such conditions, the loss of weight in the anode was 13.38 grams, while the gain of weight in the cathode was 13.82 grams, representing a plating efficiency of approximately 96.82%.

It is to be noted that the cyanide-to-metals ratio preferably maintained in the bath is lower than that conventionally considered to be desirable in cyanide electrolytes. The recommended ratio, however, is found, in the method of the present application, to produce a higher rate of deposition, and to result in a brighter and better color than can be obtained with higher ratios.

Sometimes, after extended periods of operation, the plating solution is found to become opalescent and dark. This condition can be rectified either by reversing the current flow, using a steel anode, or by the addition of a very small amount of hydrogen peroxide on the order of two drops of 30% hydrogen peroxide to approximately five liters of electrolyte.

The resistance of the plated deposit to corrosion has been determined by carefully conducted tests in which strips plated according to the present process were subjected to salt spray. Under those tests, a strip carrying a deposit 0.0003'' thick failed after 1466 hours, while similarly plated strips carrying deposited thicknesses of 0.0004'' and 0.0005'' were not completely broken after 1466 hours of subjection to the salt spray. In still another test, a similar strip plated to the thickness of 0.00015'' was subjected to the salt spray, and it was found that the first break occurred after 144 hours of such exposure.

I claim as my invention:

1. The method of producing a corrosion-resistant plated surface on a platable article which comprises the steps of immersing in a bath comprising an aqueous solution of zinc, copper and tin salts, and containing an alkali cyanide and a caustic alkali, a cathode to be plated and an anode comprising an alloy of zinc approximately 90%, copper approximately 8.5% and tin approximately 1.5%, and passing through said bath between said electrodes, a plating current, the metal components of said salts being present in the bath substantially in the proportions in which the corresponding metals are present in the said anode.

2. The method of claim 1 in which, per gallon of water, the dissolved substances are:

	Ounces
Sodium hydroxide	6.5–9
Sodium cyanide	3–13.5
Zinc cyanide	6.5–11
Cuprous cyanide	0.5–2
Potassium stannate	0.1–0.3

3. The method of claim 1 in which, per gallon of water, the dissolved substances are:

	Ounces
Sodium hydroxide	8
Sodium cyanide	4.07
Zinc cyanide	9.89
Cuprous cyanide	0.70
Potassium stannate	0.23

4. The method of claim 1 in which, per gallon of water, the dissolved salts of metals contained in the anode are:

	Ounces
Zinc cyanide	6.5–11
Cuprous cyanide	0.5–2
Potassium stannate	0.1–0.3

5. The method of claim 1 in which the current density is maintained in the range between 25 and 45 amperes per square foot of immersed cathode surface.

6. The method of claim 1 in which the temperature of the bath is maintained in the range between 70° and 140° F.

7. The method of claim 1 in which the plating current is maintained approximately at 3.8 volts and 35 amperes per square foot of immersed cathode surface, and the temperature of the bath is held between 70° and 140° F.

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