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PLATING

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This invention relates to the electroplating of metallic members and, more particularly, to the electrodeposition on members of a plurality of layers of metals whose properties are correlated to give excellent corrosion resistance and a high resistance to abrasion and wear.

In applying chromium as an electrodeposited coating to metal surfaces, it is well-known that, while chromium plate possesses extreme hardness and desirable color, the corrosion resistance is insufficient for most purposes and some other metal must be applied underneath the chromium to provide for adequate protection against corrosion. It is also a fact that the appearance of electrodeposited chromium coatings is affected in a marked manner by the nature of the surface to which it is so applied.

In the art of electrodepositing chromium, it has been established for some time that the best composite electroplated coating with chromium as the outer layer upon a base metal member, particularly ferrous metals, is the combination of an initial layer of electrodeposited copper upon which a layer of nickel from about 0.5 to 1 mil in thickness is electrodeposited, and finally a layer of chromium usually of a thickness of less than 0.1 mil. The copper and nickel coatings may vary in thickness, but the order of plating is almost invariably in the order as described. In order to produce satisfactorily bright chromium plating in this combination, it has been found necessary to buff and polish the nickel plate, otherwise the chromium is dull in appearance, or will have a milky cast. While it has been proposed to reduce the amount of labor in this connection by treating the nickel plate electrolytically or chemically to impart to it a suitably bright appearance, this has not resulted in entirely satisfactory chromium plate. Therefore, the major amount of chromium-plated metal produced today is applied over buffed and polished nickel coatings.

In buffing the thin nickel plate, serious difficulties are encountered. The buffing must be conducted with great care, to avoid cutting through the nickel coating. In objects having reentrant angles and objects of complex shape in general, buffing is a tedious and costly expedient. Therefore, quantity production chromium plating applied over coatings of copper and nickel on a ferrous base frequently exhibits rust spots after a short exposure to the outdoor atmospheres. Likewise, the chromium plating often exhibits a low degree of luster. When subjected to normal wear and tear, this electroplated combination of metals often peels and wears prematurely.

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An object of this invention is to provide for applying to metallic members a protective electrodeposited coating composed of an alloy of copper, tin and zinc, in combination with an outer coating of chromium, the whole characterized by great brilliancy and hardness.

Another object of the invention is to provide for applying to members a protective electrodeposited coating of brass followed by a coating of an alloy of copper, tin and zinc and an outer coating of chromium for securing a high degree of corrosion resistance, hardness and brilliancy.

A further object of the invention is to provide for applying a balanced composite electroplate of a ternary alloy of copper, tin and zinc, having extraordinary throwing power to balance an outer electrodeposit of chromium lacking high throwing power.

Other objects of the invention will, in part, be obvious and will, in part, appear hereinafter.

According to the present invention, metallic base members, when coated with a thin electrodeposited layer of a ternary alloy composed essentially of from 50% to 75% copper, 20% to 35% tin and 8% to 15% by weight of zinc, have a brilliant silvery appearance without buffing or polishing, and are suitable for the direct application of an electrodeposited layer of chromium thereon. The chromium applied in this combination is of brilliant appearance. The composite coating is unequalled by any other known plating of equal thickness with regard to its corrosion resistance, brilliancy of color, and resistance to abrasion and wear. The ternary alloy plate balances any unsatisfactory features of chromium plate and cooperates to enhance the best properties of chromium. Furthermore, for an equivalent corrosion resistance, the total thickness of the ternary alloy and chromium may be thinner than that of any known combination involving nickel and chromium.

In practicing the invention, various metallic base members may be treated. Ferrous metals of all kinds, brass, bronze and copper alloys, copper, nickel, cadmium, cobalt, tin, zinc, and alloys of these and other metals may be provided with the composite electroplated coatings described herein. The metal base members are thoroughly cleaned before being electroplated. Solvent degreasing or alkaline washing, preferably electrolytically conducted, are two suggested methods of securing a clean surface. In some cases, acid etching may be resorted to, to insure a satisfactory surface cleanliness. Where the surface of the metal is covered with scale, rust,

or other corrosion products, it is desirable initially to sandblast, buff with a wire wheel, sand or grind the metal surface, or otherwise mechanically remove the deleterious coating and then chemically clean the surface. A chemically clean surface is required in accordance with well-established principles of electroplating.

For ferrous base metals, it may be desirable to initially deposit a thin coating of copper prior to applying thereto the electrodeposit of ternary alloy. A plating of copper of from less than 0.1 mil to 1 mil in thickness, or even more in some cases, has been found to impart some benefit.

For ferrous metals an initial coating of brass has been found to produce unusually good corrosion resistance. For equal thicknesses a 60–40 brass coating in the present combination gives about triple the corrosion resistance as compared to a copper coating. Brass is applied in a thickness of from 0.1 to 5 mils. A thickness of 0.5 mil has given good results.

Brasses of various copper content, particularly of over 50% copper and the remainder mainly zinc are suitable for this invention. Small amounts of other metals such as tin may be present in the brass.

The cleaned metal base member, with or without a copper or brass coating, is made the cathode and suspended in an electrolyte for depositing the bright silvery ternary alloy of copper, tin and zinc from an anode thereof. One bath for carrying out this plating has the following constituents:

Free cyanide	0.5 ounce to 5.0 ounces per gal.
Copper	0.2 ounce to 0.4 ounce per gal.
Tin	0.05 ounce to 0.20 ounce per gal.
Zinc	0.1 ounce to 0.5 ounce per gal.
Sodium carbonate	2.0 ounces to 8.0 ounces per gal.
Sodium hydroxide	About 0.25 ounce per gallon to give a pH of from 12 to 12.6

When the composition is maintained within the limits indicated, plating of the ternary alloy of copper, tin and zinc may be accomplished with satisfactory results. To secure an electroplating bath of the above composition, the following chemicals in the indicated quantities may be added per 1000 parts of water:

	Parts
Copper cyanide	2 to 4
Sodium cyanide	4 to 40
Zinc cyanide	3 to 8
Sodium stannate	1.5 to 2½
Sodium carbonate	15 to 70

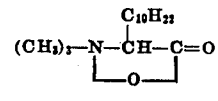
Zinc may be added as zinc sulfate. Other zinc, tin and copper salts, which are soluble in a cyanide solution may be employed in preparing the electrolyte. It will be understood that potassium salts may be used instead of sodium salts, allowance being made for the difference in molecular weight. The electrolyte is prepared by dissolving the finely powdered salts in the predetermined quantity of water.

The ternary alloy which is electroplated in practicing the present invention may consist of from 50% to 75% copper, 15% to 35% tin, and 5% to 15% zinc. In some cases, these proportions may be departed from to a slight extent. The presence of minor amounts of other metals or impurities is believed not to affect the nature of the electroplated product. Particularly good results are obtained if the copper content is from 60% to 65%, the tin from 20% to 35% and the zinc from 8% to 15%.

Plating of the ternary alloy may be carried out with inert anodes of graphite and the solution metals replenished from time to time. However, best results are secured with soluble alloy anodes. The anodes employed in the electroplating bath of the ternary alloy are composed of from 50% to 75% of copper, 20% to 35% tin and 5% to 15% by weight of zinc. A slightly higher tin content is not a disadvantage, since during the electroplating operation, a small fraction of the tin will precipitate out of the electrolyte as a sludge.

The electroplating of the ternary alloy in the electrolyte of the above composition may be carried out with greatly improved results if addition agents are added to the electrolyte. A brighter electroplate may be secured if from 0.5 to 2 ounces per gallon of an alkali metal thiocyanate is added. Potassium or sodium thiocyanates are examples of suitable brighteners.

It has been discovered that the electrodeposit is rendered more continuous whereby a more corrosion resistant coating is produced with less pitting if betains are added to the electrolyte. Betains generally include the N-trialkyl derivatives of amino acids. For the purpose of this invention, betains which have had the best results are those which have at least one non-cyclic hydrocarbon radical containing 10 to 20 carbon atoms. For example, trimethyl-C-cetyl alpha betaine is a suitable addition agent. Trimethyl-C-decyl alpha betaine, also usable in this invention, has the following accepted formula:



The betaines which may be employed in the practice of my invention are numerous and well-known and need not be listed in detail.

The proportion of betaine which has produced the most satisfactory results is from 0.01 to 1 ounce per gallon of the electrolyte. From time to time, small amounts of the betaine should be added in order to replace drag-out losses as plating proceeds.

In general, the betaines and thiocyanate are fully compatible and stable with the various addition agents and the constituents of the plating bath. The bath or electrolyte is operated at a pH of from between 11 and 13.5, preferably at a pH of about 12.5 to 13.0.

In electroplating an alloy composed of 60%–65% copper, 20%–35% tin, and 8%–15% zinc, for example, to produce a white silvery plate, the voltage between the anode and cathode should be maintained within the limits of 3 to 5 volts where the anodes and cathodes are separated at standard plating distances of the order of 4 to 8 inches. A higher voltage will be required if the anodes and cathodes are separated by more than such standard distance.

The ternary alloy is extremely brilliant when electroplated from a bath directly upon the base member. No buffing is necessary or required. Tests of its reflectivity indicate that it has approximately 85% of the reflectivity of freshly electroplated silver. Its brightness is permanent; base members plated with the ternary may be stored or handled in the shop for some period

of time before further processing, without deterioration of the brightness of the ternary alloy coating.

After having been plated with the ternary alloy, preferably in the range of from 0.1 mil to 0.5 mil in thickness, with 0.2 mil thickness being an optimum, the plated member is then electroplated in a conventional chromium plating bath such, for example, as one containing in the neighborhood of 250 grams per liter of chromic acid (CrO_3) and 2½ grams per liter of sulphuric acid. The patent to Fink, 1,802,463, discloses bath compositions and the operating conditions suitable for producing a bright chromium plate on members. Other processes for producing bright chromium plate can also be employed. It is preferred that the chromium plating bath be so regulated as to produce on the ternary alloy coating a plate of mirror-like chromium.

The ternary alloy of copper, tin and zinc has an extremely high degree of hardness, much higher than that of normal nickel plate and, therefore, is adapted to cooperate better with the extremely hard chromium electroplated coating than nickel does in the conventional nickel-chromium coatings. The combination of the ternary alloy and chromium is superior to nickel-chromium in wear resistance and abrasion resistance, as determined by the Taber abrasion tester. Salt-spray tests and humidity cabinet tests of the ternary alloy and chromium composite coatings on ferrous metal show that the combination surpasses any standards required for chromium plating. Comparative tests further indicate that the corrosion resistance exceeds that of any previous combination employing chromium for coatings of total equal thickness.

A particularly outstanding advantage of the ternary alloy and chromium combination of composite metals is that the ternary alloy electrolyte has outstanding throwing power and the alloy plate has extraordinary penetrating power. The ternary alloy is readily deposited in deep recesses and cracks. Hollow tubes and similarly difficult plateable members may be readily plated, often without special anodes or similar means normally required to deposit metal in such recesses or bores. By comparison, chromium plating is notoriously difficult to plate in recesses and other re-entrant types of surfaces. Special anodes and thieves are required to insure a uniform and properly applied coating of chromium. Owing to the hardness and brilliancy of the ternary alloy, it is not so critical that the cromium plate adequately cover deep recesses, since the ternary alloy deposited therein will appear and wear to a great extent like chromium. The extreme hardness of chromium metal obviously is needed most on exposed and projecting surfaces, where it normally tends to plate out most efficiently. The combination of the ternary alloy with chromium as a composite plate therefore balances any weaknesses of chromium and gives an overall outstanding metal plate.

Since certain changes in carrying out the above processes and certain modifications in the compositions which embody the invention may be made without departing from its scope, it is intended that all the matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

I claim as my invention:

1. An article of manufacture comprising, in combination, an electrically conducting base member, a thin electrodeposited coating of a thickness of from 0.1 to 0.5 mil of a bright silvery ternary alloy composed of from 50% to 75% copper, 20% to 35% tin and from 8% to 15% zinc applied to the base member, and a thin coating less than 0.1 mil in thickness of chromium electrodeposited over the ternary alloy coating.

2. An article of manufacture comprising, in combination, a ferrous base member, a thin electrodeposited coating of a thickness of from 0.1 to 0.5 mil of a bright silvery ternary alloy composed of from 50% to 75% copper, 20% to 35% tin and from 8% to 15% zinc applied to the base member, and a thin coating less than 0.1 mil in thickness of chromium electrodeposited over the ternary alloy coating.

3. An article of manufacture comprising, in combination, a ferrous base member, an electrodeposited coating of copper applied to the ferrous base member, a thin electrodeposited coating of a bright silvery ternary alloy composed of from 50% to 75% copper, 20% to 35% tin and from 8% to 15% zinc applied to the copper coating on the base member and a thin coating of chromium electrodeposited over the ternary alloy coating.

4. An article of manufacture comprising, in combination, a ferrous base member, and electrodeposited coating of brass composed of over 50% copper and the balance being zinc, applied to the ferrous base member, a thin electrodeposited coating of a bright silvery ternary alloy composed of from 50% to 75% copper, 20% to 35% tin and from 8% to 15% zinc applied to the brass coating on the base member and a thin coating of chromium electrodeposited over the ternary alloy coating.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,615,585	Humphries	Jan. 25, 1927
1,651,278	Humphries	Nov. 29, 1927
2,181,773	Wernlund	Nov. 28, 1939
2,198,365	Cinamon	Apr. 23, 1940

OTHER REFERENCES

Metals Handbook, 1939 ed., pp. 1481–1482.
Eng. Alloys, p. 258.