ELECTROLESS DEPOSITION OF NICKEL-PHOSPHORUS BASED ALLOYS
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10 Claims

ABSTRACT OF THE DISCLOSURE

Articles of manufacture made from a basis metal having an electrolessly deposited nickel-phosphorus based alloy coating thereon, the alloy containing from more than 1% to about 45% of an element which is codeposited with the alloy, the element being tungsten, rhodium, beryllium, rhodium, palladium, platinum, tin, zinc, molybdenum or gold. The nickel predominates the phosphorus in quantity.

The invention described herein may be manufactured and used by or for the Government for governmental purposes without the payment to one of any royalty thereon.

This invention is a divisional application of my copending application Ser. No. 407,941, filed Oct. 30, 1964, for "Electrolese Deposition of Nickel-Phosphorus Based Alloys," now abandoned and relates to electrolese deposition and more particularly concerns the electrolese deposition of nickel-phosphorus alloys containing tungsten, zinc, tin, rhodium and molybdenum.

Nickel coatings have long been used for improving the appearance of steel products and yet protecting the basis metal from harmful or corrosive attacks. Until recently, nickel plating was accomplished by an electrodiposition process which suffered essentially in the poor throwing power of the electrodiposed nickel making it difficult to achieve uniformly of coating on irregularly shaped objects.

In the prior art, a chemical nickel plating process was developed based on the reduction of nickel salts by hypophosphite, and is represented approximately by the following reaction:

\[ \text{N}^{1+} + 2\text{HPO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{N}^{1+} + 2\text{H}_2\text{PO}_4^{2-} + 4\text{H}^+ + 2\text{H}_2 \]

The electrolese deposition of nickel, or more correctly, nickel-phosphorus alloys, occurs wherever the basis metal is in contact with the electrolese plating solution and provides excellent deposition uniformity. I have plated numerous small, intricately shaped metal components, such, for example, as timing mechanisms, very successfully, with the electrolese process, whereas the electrodiposition process was ineffective in plating such mechanisms. Similarly, the interiors of long, narrow tubes can readily be plated with the electrolese nickel process whereas it is virtually an impossible task to be accomplished by standard electrodiposition methods. Further, the hardness of electrolese deposited nickel is greater than that of electrodiposed nickel and can be further increased by additional heat treatment. A further interesting feature of electrolese deposited nickel resides in the fact that it can be readily applied directly over properly activated non-conductors. However, the prior art electrolese technique is restrictive in that very few metals can be deposited thereby. In addition, there are many applications wherein improved tarnish resistance, to acid attack, ductility, corrosion protection of a basis metal, high temperature oxidation resistance and wear resistance would be desirable.

It is therefore a principal object of this invention to provide new and useful electrolese nickel-phosphorus based alloys containing other metals.

Another object of the invention is to provide bath solutions for the electrolese deposition of nickel-phosphorus alloys containing other metals.

Other and further objects of the invention will be apparent to those skilled in the art upon study of this disclosure.

Briefly, and in accordance with my invention, I have discovered that tarnish-resistant and/or corrosion-resistant alloys can be successfully electrolese plated onto the basis metals normally employed in electrolese nickel deposition.

More specifically, I have found that when sodium tungsten is added to the prior art acid-citrate electrolese nickel solution bath and the pH of the bath is raised above about 7, substantial tungsten content is detected in deposits. In order to prevent the precipitation of nickel salts at higher pH values, the concentration of the nickel salts is decreased to about 20% of the usual concentration (35 g./l. of NiSO_4·6H_2O) and the remaining 80% replaced by an atomic equivalent of tungsten obtained from sodium tungstate.

In Table I it will be seen that I have successfully electrolese plated nickel-phosphorus alloys containing tungsten from an unammoniated alkaline citrate bath solution.

| TABLE I—NICKEL-PHOSPHORUS ALLOY OF TUNGSTEN FROM UNAMMONIATED ALKALINE CITRATE BATH |
| Compound | Preferred Quantity, g/l. | Quantity, Effective Range g/l. |
| NiSO_4·6H_2O | 7 | 2-21 |
| Sodium Citrate·2H_2O | 30 | 10-40 |
| NaHPO_4 H_2O | 10 | 5-20 |
| NaWO_4·2H_2O | 25 | 6-80 |

The effective range of pH is between 7 and 10 although a pH of 8.2 is preferred. The bath temperature range is between about 90 to 100° C. with 98° C. being most desirable. The amount of tungsten in the electrolese deposit is about 15% with the balance being about 94% nickel and 6% phosphorus when using the preferred bath of Table I above.

Similarly, I have found that tin, zinc, rhodium, beryllium and rhodium may be electrolese deposited with the nickel-phosphorus when the appropriate metal salt is used in place of sodium tungstate in the example of Table I above. See Table II.

| TABLE II |
| Compound Dissolved in Bath | Preferred Quantity in Bath, g/l. | Metal Deposited Approximate Cost of Metal in Deposit, percent |
| NaSnO_2·2H_2O | 1.4 | Sn | <1 |
| BiSO_4·3H_2O | 1.4 | Zn | 17 |
| KIO_3 | 1.6 | Re | 17 |
| BiCl_3·2H_2O | 0.2 | Co | - |
| RhCl_3·3H_2O | 0.2 | Rh | 12 |

Note.—All bath solutions were operated at 95° C. and pH=8.2.

These alloys however require that the bath solution be stabilized against decomposition such as by the addition of about 0.2 ml./l. of a solution of 10 g./l. of mercaptobenzozazole in 2 N NaOH.

In addition, I have found that a number of metals, including rhodium, zinc, molybdenum and tin, can be co-deposited with nickel-phosphorus using an ammoniated alkaline citrate bath. See the examples of Table III.
The preferred pH for the electrolytic plating from the ammoniated alkaline citrate bath is 9.0 at a bath temperature of 98° C. The effective pH and temperature ranges will be about 8 to 10 and 90 to 100° C, respectively. The pH is maintained by periodic additions of NH₄OH. Further, any combination of tungsten, tin, rhenium, zinc and molybdenum may be co-deposited electrolytically with nickel-phosphorus. For example, nickel-phosphorus-rhenium-tungsten may be electrolytically deposited from both an unammoniated and an ammoniated alkaline citrate bath.

Salt spray corrosion tests were performed on steel panels coated with 0.3 mil of some of the deposits shown in Tables I and III. My nickel-phosphorus-tin and nickel-phosphorus-rhenium deposits exhibited superior corrosion protection of the steel substrate as compared to the standard electrolytic nickel deposit. My nickel-phosphorus-tin and particularly my nickel-phosphorus-tungsten deposits provided superior tarnish resistance qualities.

Acid resistance tests performed on the aforementioned panels revealed that my nickel-phosphorus-tungsten deposit has superior resistance to 50% nitric acid attack over conventional electrolytic-nickel coated panels.

The nickel-phosphorus-zinc coating was found to be 100 millivolts more active in potential than conventional electrolytic nickel deposits. This property is useful for sacrificial protection of certain metals.

It is apparent that in the foregoing description of my invention, new bath compositions are described for yielding electrolytic deposited alloys which are useful for providing superior corrosion protective properties to a basis metal and for imparting excellent tarnish resistant properties thereto.

I claim:

1. An article of manufacture comprising a basis metal structure having an electrolytic deposited coating thereon, said coating consisting essentially of an alloy of nickel, phosphorus and at least one element selected from the group consisting of tungsten, molybdenum, rhenium, beryllium, rhodium, palladium, and platinum, said alloy being characterized as a nickel-phosphorus based alloy wherein nickel is present in major proportions and phosphorus is present in minor proportions, and wherein said element is present in an amount ranging between greater than 1% to about 45%.

2. An article according to claim 1 wherein said element comprises tungsten.

3. An article according to claim 1 wherein said element comprises molybdenum.

4. An article according to claim 1 wherein said element comprises rhenium.

5. An article according to claim 1 wherein said element comprises beryllium.

6. An article according to claim 1 wherein said element comprises rhodium.

7. An article according to claim 1 wherein said element comprises palladium.

8. An article according to claim 1 wherein said element comprises platinum.

9. An article according to claim 2 wherein said tungsten comprises at least 13% by weight of said coating.

10. An article according to claim 4 wherein said rhenium comprises at least 45% by weight of said coating.

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