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PALLADIUM-NICKEL ALLOY PLATING BATH

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No Drawing. Continuation-in-part of application Ser. No. 695,576, Jan. 4, 1968, now Patent No. 3,580,820. This application Apr. 22, 1971, Ser. No. 136,588

Claims priority, application Japan, Jan. 11, 1967, 42/1,868

Int. Cl. C23b 5/32, 5/46

U.S. Cl. 204—43 3 Claims

ABSTRACT OF THE DISCLOSURE

A palladium-nickel alloy plating bath is formed of a solution of a palladium salt and a nickel salt in ammonia, and a brightener in the nature of a sulfonamide is added to the bath in which a metal is plated for approximately 30 minutes at a pH between 7 and 10, temperature between 15° C. and 40° C., and a cathode current density of 0.5 to 1.5 a./dm.^{2} without agitation.

CROSS-REFERENCE TO RELATED APPLICATION

The present application is a continuation-in-part of the application bearing the serial number 695,576, now Pat. No. 3,580,820. The inventors are the same in both applications.

BACKGROUND OF THE INVENTION

Methods of plating palladium were originally developed with the objective of eliminating some of the drawbacks of conventional light metal plating where the deposits consisted of silver or nickel. However, palladium coatings of a thickness great enough to give adequate corrosion resistance and wear resistance are expensive, so that it would be desirable to find a method of depositing a less expensive but sufficiently protective coating which in addition would have a mirror finish.

SUMMARY OF THE INVENTION

According to the present invention, a bath with a pH between 7 and 10, containing aqueous ammonia, palladium ions and nickel ions, and an aromatic sulfonamide yields an electrodeposited coating which is an alloy of palladium and nickel and which has a bright mirror finish. The coating is essentially as corrosion and wear resistant as is palladium itself.

Accordingly, an object of the present invention is to provide a bath from which a coating can be electrodeposited which is an alloy of palladium and nickel.

Another object of the invention is to provide a bath from which an alloy of nickel and palladium can be deposited where the deposit has a bright mirror finish.

Still other objects and advantages of the invention will in part be obvious and will in part be apparent from the specification.

The invention accordingly comprises a composition of matter possessing the characteristics, properties, and the relation of components which will be exemplified in the composition hereinafter described, and the scope of the invention will be indicated in the claims.

PREFERRED EMBODIMENTS OF THE INVENTION

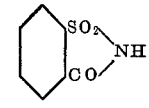
Generally, palladium salts and nickel salts are soluble in aqueous ammonia to form ammine-complex salts wherein the metal atom is coordinated with NH_3. Stable complex salts are formed regardless of the nature of the acidic radical used. In accordance with the invention, it has been found that when using a bath comprising ammine-complex salts of palladium and nickel, that palladium and nickel codeposit in the form of a solid solution alloy. It was also found that the addition of an aromatic sulfonamide would cause the deposit to have a bright mirror finish. Further examination revealed that the palladium content in the codeposited layer can be established at any point within the range of 30% and 90% by adjusting the composition of the bath or plating conditions and that the thus-plated surface obtained shows sufficient brightness and corrosion-resistance.

In preparing a bath for plating, a monosalt such as palladium chloride, $PdCl_2$, or a complex salt such as diammine palladium chloride, $Pd(NH_3)_2Cl_2$, can be used as sources of palladium. As for sources of nickel, nickel sulfate, $NiSO_4 \cdot 7H_2O$, nickel chloride, $NiCl_2 \cdot 6H_2O$, etc. are used. When these salts are put in an aqueous solution of ammonia, the palladium and nickel salts are converted into ammine-complex salts. An ammonium salt of inorganic acid or organic acid such as ammonium sulfate or ammonium citrate may be added. These additions increase the solubility of palladium and nickel, by which stable dissolution at relatively low pH is achieved. The electroconductivity of the bath is also improved and at the same time the pH is stabilized by the NH_4^+-NH_3 buffer system produced in the bath. The concentration of palladium and nickel in the bath is controlled in such a manner that the quantity of palladium present is 5 to 30 g./l., and nickel is present in the same quantity, i.e., 5 to 30 g./l. The ratio of palladium and nickel in the deposited layer depends on the concentration ratio of palladium and nickel in the bath. For instance, a combination of 20 g./l. of palladium and 10 g./l. of nickel produces an alloy deposited layer comprising palladium in the amount of 85%, and an alloy deposited layer composed of 60% of palladium is obtained with a combination of 10 g./l. of palladium and 10 g./l. of nickel. Although it is not only the concentration ratio of palladium and nickel that affects the composition of the alloy deposited layer, nevertheless, other conditions such as pH of the bath, the temperature and cathode current density need cause no concern because it is easy to keep these conditions constant during the plating operation, and except for the pH of the bath, changes in the other conditions do not affect the product adversely. Therefore, the desired codeposited layer can be obtained if the concentration of palladium and nickel in the bath and the ratio thereof are controlled.

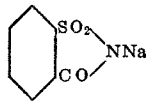
By adding aromatic sulfonamides to the bath, a bright plating can be obtained. Discovery of these brighteners gives the bath great practical value.

Examples of aromatic sulfonamides that can be used are:

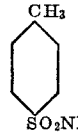
(1) Saccharin



(2) The sodium salt of saccharin



(3) Para-toluenesulfonamide



Example 1

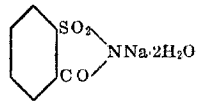
Saccharin was used as follows:

A bath containing 40 g. of diammine palladium (II) sulfate, $Pd(NH_3)_2SO_4$, 50 cc. of 28% aqueous ammonia, and 650 cc. of water was prepared. To this were added 50 g. of ammonium sulfate, 25 g. of nickel chloride and 1 g. of saccharin, and the bath was made up to 1000 cc. with water.

A brass test piece was plated in this bath for 30 minutes at a pH of 8.4, temperature of 25° C. and current density of 1 a./dm.^{2} without agitation. The electrodeposit contained 80% of palladium and 20% of nickel and had a mirror surface. The deposit was unaffected by 24 hours exposure to ammonia gas and by 6 days immersion in artificial seawater.

Example 2

A bath containing 40 g. of diammine palladium chloride, $Pd(NH_3)_2Cl_2$, 50 cc. of 28% ammonia water and 700 cc. of water was prepared. Then were added 50 g. of ammonium sulfate, 50 g. of nickel sulfate, 5 g. of sodium saccharate



and water until the bath attained 1000 cc.

A brass test piece was plated in the bath for 30 minutes at pH of 8.8, temperature of 30° C., and cathode current density of 1 a./dm.^{2}, without agitation.

An alloy comprising 85% palladium and 15% nickel with a mirror surface was obtained from this bath. The deposit was unaffected after 24 hours exposure to ammonia gas and 6 days immersion in artificial seawater.

Example 3

Para-toluenesulfonamide was used as follows:

A bath containing 20 g. of diammine palladous chloride, 50 cc. of 28% aqueous ammonia and 700 cc. of water was prepared. To this were added 50 g. of ammonium sulfate, 35 g. of nickel sulfate, 0.5 g. of para-toluenesulfonamide, and water to bring the final volume to 1000 cc.

A brass test piece was plated in this bath for 30 minutes at a pH of 8.4, temperature of 30° C., and a cathode current density of 1 a./dm.^{2} without agitation. An alloy comprising 80% palladium and 20% nickel with a mirror finish was deposited. The deposit was unaffected by exposure to ammonia and seawater as described in the previous example.

Composition and internal stress of the deposited layer show no noticeable change by this bright plating. Satisfactory results can be obtained when the bath is operated at pH 7–10, temperature 15–40° C., cathode current density 0.5–1.5 amperes/dm.^{2}, using a palladium or a graphite anode. During plating, the concentration of palladium and nickel must be estimated by chemical analysis and always controlled properly. The metals are supplied by adding the appropriate salts directly to the bath. During the plating the ammonium salt gradually accumulates in the bath but it has no deleterious effect. The pH is adjusted by adding ammonia water or dilute sulfuric acid. Generally, lowering of pH tends to make more noble the deposition potential of nickel and to increase the nickel content in the deposited layer. It sometimes occurs that the palladium content in the deposited layer does not fall within 30% and 90%, owing to improper composition of the bath or plating conditions. If the palladium content in the codeposited layer deviates substantially from the range of 30 to 90%, a solid solution of palladium and nickel is not formed completely, and when a thick plating is deposited, the surface loses its brightness and is fragile. Other plating conditions are the same as those in conventional methods. There are no restrictions as to the kind of the base metals.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained, and since certain changes may be made in the above compositions without departing from the spirit and scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

What is claimed is:

1. A palladium-nickel alloy aqueous electroplating bath having a pH between 7 and 10, comprising aqueous ammonia containing 5 to 30 g./l. of palladium ions, 5 to 30 g. of nickel ions, and an aromatic sulfonamide in an amount effective for obtaining a bright electrodeposited layer of a palladium-nickel alloy therefrom.

2. Bath as defined in claim **1**, wherein said aromatic sulfonamide is selected from the group consisting of saccharin, sodium saccharin, and para-toluenesulfonamide.

3. Bath as defined in claim **1**, wherein the quantity of said brightener added lies between 0.5 and 5 g./l.

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