



PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Palladium-Nickel Alloy Plating Bath.

We, KABUSHIKI KAISHA SUWA SEIKOSHA and NISSHIN KASEI KABUSHIKI KAISHA, both Japanese Companies, of 5—19, 4-chome, Ginza-Nishi, Chuo-ku, Tokyo, Japan and 20, Kawara-machi, Senju, Adachi-ku, Tokyo, Japan, respectively, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the electrodeposition of palladium alloys and more particularly to the electrodeposition of palladium-nickel alloys and to plating baths for use in such electrodeposition.

Because conventional plating with silver or nickel has certain disadvantages it has in recent years been proposed to electroplate articles with palladium. However, this is a somewhat expensive form of plating and it is an object of the present invention to provide plating baths which serve to deposit platings of palladium-nickel alloy of high corrosion resistance and which reduce the plating costs (as compared with the plating of palladium per se). By reason of the advantages in cost obtained it is possible to employ the plating baths of the present invention in a wide range of applications while still maintaining the process on an economical basis.

According to the present invention there is provided a plating bath for electrodeposition of a palladium-nickel alloy which comprises an aqueous solution of palladium and nickel amines, the content of palladium in said solution being from 5 to 30 grams per litre, the content of nickel in such solution being from 5 to 30 grams per litre and the relative proportions of the palladium and nickel being such that the palladium nickel alloy deposited from said solution by electrodeposition has a palla-

dium content of 30 to 90% by weight of the alloy.

According to a further feature of the present invention there is provided a process for the production of electroplatings of palladium-nickel alloys which comprises subjecting to electrodeposition a plating bath as just defined.

Generally speaking palladium salts and nickel salts are each soluble in aqueous ammonia solution with the formation of coordination complexes known as amines. The nature of the anion of the palladium and nickel salts used to form the amines is in no way critical and it is bound into the stable ammine complex salts produced. The most convenient sources of the palladium and nickel are their simple salts such as palladium chloride PdCl_2 , nickel sulphate $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and nickel chloride $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. When these salts are added to aqueous ammonia the ammine salts are formed in solution. By including in the solution an ammonium salt of an organic or inorganic acid, such as ammonium sulphate or ammonium citrate, the solubility of the palladium and nickel salts may be increased and a stable solution obtained at lower pH values. Further, the electroconductivity of the bath is improved, and the pH stabilised, by including in the bath an $\text{NH}_4^+/\text{NH}_3$ buffer system.

Of course it will be appreciated that the bath may also be formed by the dissolution together of the preformed palladium and nickel amines.

As noted above the quantities of the palladium and nickel salts used should be such as to establish in the bath palladium and nickel concentrations each within the range of 5 to 30 grams per litre. Further, as noted above the relative proportions of the palladium and nickel should be such that on electrodeposition the plated-out alloy

contains 30 to 90% by weight of palladium. In this connection it may be noted, by way of example, that if palladium and nickel are present in the bath each at a concentration of 10 grams per litre, the electrodeposited alloy has a palladium content of about 60% by weight: if the concentrations are changed to 20 grams per litre of palladium and 10 grams per litre of nickel, the electrodeposited alloy has a palladium content of about 85%. The precise composition of the electrodeposited alloy may be affected also by other factors, such as the pH of the bath, the temperature and the current density used but these are factors under the users control and may be held constant so that a desired alloy constitution is achieved. Of the factors just mentioned only the pH of the bath has any important effect.

Plating baths as just described can be used to afford bright palladium/nickel alloy deposits but the brightness of the deposit can be enhanced by adding brighteners e.g. those known *per se* as brightening agents in nickel plating baths. In particular, in accordance with the present invention the baths may contain naphthalene sulphonic acid salts or aromatic sulphonamides as brightening agents. Suitable such compounds are the salts of naphthalene sulphonic acids irrespective of the number of sulphonic acids present and their nuclear substitution positions. The acids are most conveniently used as sodium salts and examples are the sodium salts of naphthalene α - and β -sulphonic acids, naphthalene 1,5-disulphonic acid and naphthalene 1,3,6-trisulphonic acid.

Examples of suitable aromatic sulphonamides are saccharin (*o*-sulphobenzoic acid imide) and *p*-toluene-sulphonamide but generally aromatic compounds containing the characteristic $-\text{SO}_2\text{NH}-$ group may be employed.

The presence of the brightening agents referred to above has no important effect on the composition or mechanical properties of the electrodeposited alloy plating.

In effecting electro-plating by the use of a plating bath according to this invention, it is found generally to be preferable to operate at a bath pH of 7 to 10, a temperature of 15 to 40°C a cathode current density of 0.5 to 1.5 amp/square decimetre and to use a palladium or graphite anode.

To maintain control over the plating process analyses of the plating bath should be effected at suitable intervals. Deficiency metal shown by such analyses can be replenished by adding the metal salt directly to the bath. During plating the bath accumulates ammonium salts but this has no seriously deleterious effects. Departure of the pH of the bath from the desired level can be compensated by adding aqueous am-

monia or dilute sulphuric acid to the bath. Generally, the effect of working at a lower pH is to increase the deposition potential of nickel and to increase the nickel content in the electrodeposited alloy.

It may be observed that if the conditions in the plating bath are allowed to vary so widely from the conditions herein set forth that the palladium content of the electrodeposit is outside the range of 30 to 90% referred to above, then the desired solid solution (alloy) of palladium and nickel is not completely formed with the result that a thick deposit will lack brightness and become brittle.

The method of electrodeposition referred to herein may be employed to provide a palladium nickel alloy coating on any electrically conductive surface. Generally the article being plated will be of metal, the metal itself being in no way critical.

EXAMPLE 1

A bath containing 20 g of palladous ammine chloride $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$, 50 cc of 28% aqueous ammonia and 700 cc of water was prepared. Ammonium sulphate (50 g), nickel sulphate $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (50 g) and water sufficient enough to form 1000 cc were then added.

A brass test piece was plated in said bath for 30 minutes at pH 7.5, temperature 30°C, and cathode current density 1A/dm², without agitation.

An alloy electroplating comprising palladium 60% and nickel 40%, with a white bright surface was thus obtained and the deposited layer adhered well to the base.

EXAMPLE 2

There was added to the bath described in Example 1 10 g of sodium 1,3,6-naphthalene trisulphonate and plating was effected as in Example 1.

The electrodeposited layer having a thickness of 10 μ , had a mirror polished surface and a hardness Hv, tested by the Vickers hardness tester, of Hv=535.

The electrodeposited layer was found to be unaffected by exposure to ammonia gas for 24 hours and by immersion in artificial sea water for 6 days.

EXAMPLE 3

A bath containing 40 g of palladous ammine chloride $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$, 50 cc of 28% aqueous ammonia and 700 cc of water was prepared. Ammonium sulphate (50g) nickel sulphate (50g), the sodium salt of saccharin ($2\text{H}_2\text{O}$) (5g) were added, together with sufficient water to take the volume of the bath to 1 litre.

A brass test piece was plated in said bath for 30 minutes at pH 8.8, temperature

30°C, and cathode current density 1A/dm², without agitation.

An alloy electroplating comprising palladium 85% and nickel 15% with a mirror polished surface was obtained. The electro-deposited layer was found to be unaffected by exposure for 24 hours to ammonia gas and by immersion for 6 days in artificial sea water.

10 WHAT WE CLAIM IS:—

1. A plating bath for electrodeposition of a palladium-nickel alloy which comprises an aqueous solution of palladium and nickel amines, the content of palladium in such solution being from 5 to 30 grams per litre, the content of nickel in such solution being from 5 to 30 grams per litre and the relative proportions of the palladium and nickel being such that the palladium nickel alloy deposited from said solution by electrodeposition has a palladium content of 30 to 90% by weight of the alloy.

2. A plating bath according to claim 1 which comprises a soluble salt of a naphthalene sulphonic acid.

3. A plating bath according to claim 1 which comprises a soluble aromatic sulphonamide.

4. A plating bath according to claim 3 wherein the aromatic sulphonamide is saccharin or *p*-toluene sulphonamide.

5. A plating bath according to any of

claims 1—4 which includes an ammonium salt of an organic or inorganic acid.

6. A plating bath according to claim 1 substantially as hereinbefore described with reference to any one of the foregoing specific Examples 1—3. 35

7. A process for the production of electroplatings of palladium-nickel alloys which comprises subjecting to electrodeposition a plating bath as defined in any of claims 1—5. 40

8. A process according to claim 7 wherein the pH of the bath is 7 to 10 the temperature is 15—40°C and the cathode current density is 0.5 to 1.5 amps/square decimetre. 45

9. A process according to claim 7 or 8 wherein the anode is of palladium or graphite. 50

10. A process according to claim 7 substantially as hereinbefore described with reference to any one of the foregoing specific Examples 1—3. 55

11. Articles having an electroplating of palladium-nickel alloy, whenever produced by the process hereinbefore described and claimed.

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