

UNITED STATES PATENT OFFICE

2,519,858

ELECTRODEPOSITION OF NICKEL AND
NICKEL ALLOYSPeter Spiro and Fritz Wohlgemuth,
London, EnglandNo Drawing. Application October 2, 1945, Serial
No. 619,904. In Great Britain September 23,
1944

6 Claims. (Cl. 204—6)

1

The present invention relates to the electro-deposition of nickel and nickel alloys upon metals and non-conductors and has for its primary object to provide an improved electrolyte which is applicable with advantage to various forms of nickel plating by electro-deposition and is particularly suitable for use in producing the thick, hard and abrasion resistant coatings of nickel and nickel alloys required in electro-forming work; such as for example the production of the surfaces of pressure moulds by electro-deposition.

Ordinary nickel deposits as usually applied in commercial nickel plating processes are unsuitable for certain industrial purposes, particularly for electro-forming work, because such deposits lack sufficient hardness. Moreover, the usual nickel bath solutions used as electrolytes for commercial nickel plating have a comparatively poor throwing power and the deposits obtained therefrom are subject to pitting and high stresses which are serious obstacles to the production of good work, especially when the deposits have to be superimposed to build up comparatively thick walls or coatings on intricate shapes; while in coating shapes formed from non-conducting materials it is essential to avoid such stresses, particularly when electro-forming surfaces of pressure moulds by providing on a master of non-conducting material shaped in accordance with the articles to be moulded, a conducting surface, prior to carrying out said electro-forming.

A nickel plating bath of the fluoride type possesses very good throwing power while plating a deposit with low stresses and we propose to use a bath of this kind in preference to other known types of nickel baths such as the "Watts," "Double salt," "Formate" and "All Chloride" types, as a basis for the invention hereinafter described.

In order to obtain harder deposits without loss of toughness and with a hardness which remains stable at temperatures above 300° C. we prefer to use a nickel depositing solution containing cobalt and we have found that the addition of cobalt to the fluoride bath increases the throwing power.

It is known that the addition of certain organic agents, e. g., 1,3,6 sodium naphthalene trisulphonate, to solutions used in the electro-deposition of bright nickel deposits increases the brightness and hardness of the deposits but the resulting coating or plating particularly if deposits of more than 20 thousandths up to 125 thousandths of an inch thickness are required is often laminated and usually very brittle, while surface

2

pitting is increased and the resulting hardness of the coating will not survive annealing temperatures above 300° C. Moreover, we have found that the addition of cobalt to a fluoride bath containing sodium naphthalene trisulphonate leads to deposition, upon the surface of the article to be coated, of an initial coating of nickel alloy which is very rich in cobalt and this cobalt-bearing coating tends to disintegrate when heated.

On the other hand, the addition of an organic agent such as sodium naphthalene trisulphonate as above described was the only means previously known to us for eliminating or substantially reducing the stresses in the electro-deposited coatings, particularly in the formation of intricate shapes by electro-deposition. As above stated the elimination of such stresses is of particular importance when coating on non-conductors and it has been found that this result is obtained by use of sodium naphthalene trisulphonate without regard to variations of current density over a wide range; moreover it applies as far as the fluoride bath is concerned to various pH values, whereas with the other known nickel baths, the result can only be obtained, if at all, at a certain critical pH value which greatly complicates the operation conditions.

The use of wetting agents to avoid pitting in electro-plating is generally known but most of the known wetting agents increase the internal stresses of the electro-deposited coatings considerably. Moreover, they are known to decompose when submitted to the usual plating conditions, i. e. when influenced by higher temperature, oxygen, development of hydrogen and associated factors and the products of the decomposition increase the stress still further, while the wetting qualities are at the same time lost.

We have now discovered that by using a fluoride bath containing cobalt with the addition of an organic hardener or brightener of the sodium naphthalene trisulphonate type, and at the same time adding a wetting agent of the type consisting of sulphonated cetyl and oleyl alcohols containing between 40-70% of the sulphonated oleyl alcohol, the remainder being sulphonated cetyl alcohol, hard and tough nickel and nickel alloy deposits can be obtained of a considerable thickness, without pits or internal stresses. We have found that the wetting agent as sold under the trade name "Claytavin WM" and formed of sulphonated cetyl and oleyl alcohols of which 40-70% is oleyl, and the rest cetyl alcohol serves well for this purpose. The hardness of the alloy

deposited from the above bath is approximately 550° Vickers. This hardness of the electro-deposit shows relative stability even at temperatures between 300° and 500° C., i. e. at temperatures used in the production of zinc and aluminium pressure die-castings. The addition of the two organic agents to the fluoride bath containing cobalt ensures hardness, stability at temperatures above 300° C., and the internal stresses, which are usually increased by wetting agents, can be substantially eliminated. An excessive cobalt deposition in the first plating period is prevented, and it is thus possible to build up a deposit of a relatively uniform nickel cobalt alloy.

Whilst the nickel electro-formed from the electrolyte of this invention is unusually stable in its hardness, even under the influence of relatively high temperatures and is not embrittled by submission to temperatures up to 300° C., a certain embrittlement sets in above 300° C., which may be mechanically disadvantageous. We have discovered, however, that by adding cadmium to the electrolyte in concentrations such as 1 in 30,000 this embrittlement is prevented, while the cadmium addition leads to a gradual increase in ductility with the subjection of the metal to increasingly high temperatures, without subsequently reducing the stability of the hardness and without reducing the absolute value of that hardness for most temperatures. It should be made clear that the physical properties of the nickel referred to are not those ruling when the nickel is subjected to the temperatures mentioned but refers to properties of the nickel at room temperature, after having been heated to certain temperatures.

The addition of the two organic agents and cadmium does not reduce the throwing power of the fluoride bath containing cobalt, which can be operated over a wider range of pH values than the usual nickel baths without reducing the stress-decreasing effect of the organic hardener.

An example of an electrolytic nickel plating bath for carrying the present invention into effect is given below:

Example

Nickel sulphate.....	ounces..	35-50
Cobalt sulphate.....	do....	1-3½
Boric acid.....	do....	4-6
Sodium fluoride.....	do....	1-2½
Sodium chloride.....	do....	¼-2
Cadmium oxide.....	grammes..	2-1

The above substances are dissolved into distilled water to make up one gallon of solution and the solution thus obtained then submitted to one of the known oxidation processes e. g. an oxidation process employing potassium permanganate to free the solution from organic and other contaminants. The solution after such processing is thoroughly filtered and the following additions are made to the filtered solution:

1-3-6 sodium naphthalene trisulphonate—4-20 grammes per gallon of solution

Sulphonated aliphatic alcohol such as sulphonated cetyl and oleyl alcohols (40-70% oleyl and the rest cetyl) (sold under the trade name Claytavin WM) 4-12 grammes per gallon of solution

The solution thus obtained should produce the results above described when used in a nickel plating bath at temperatures between 35-45° C. and at an electric current density of 8-25 amperes per square foot. The master is removed from the

bath when the deposit has reached a desired thickness, and the deposit is detached to thereby secure and form the mould.

We claim:

1. An electrolytic bath for the electrodeposition of nickel cobalt alloys upon non-conductors for electro-forming pressure molds consisting essentially in aqueous solution of 33-50 ozs. nickel sulphate, 1 to 3½ ozs. cobalt sulphate, 4 to 6 ozs. boric acid, 1 to 2½ ozs. sodium fluoride, ¼ to 2 ozs. sodium chloride, 4 to 20 grams of 1-3-6 sodium naphthalene trisulphonate and 4 to 12 grams of sulphonated aliphatic alcohol per gallon of solution.

2. An electrolytic bath for the electrodeposition of cobalt-nickel alloys upon metals and non-conductors in the production of pressure molds consisting essentially in aqueous solution for each gallon thereof 33 to 50 ozs. of nickel sulphate, 4-6 ozs. of boric acid, 1 to 2½ ozs. of sodium fluoride, 1 to 3½ ozs. of cobalt sulphate, ¼ to 2 ozs. of sodium chloride, 4 to 20 grams of an organic hardener and stress reliever having a sodium naphthalene trisulphonate base, and 4 to 12 grams of a wetting agent consisting of a sulphonated aliphatic alcohol and 0.2 to 1 gram of cadmium oxide to increase the ductility of the deposit after exposure to high temperatures.

3. A process for producing the surface of a pressure mould of nickel cobalt alloy which consists of providing on a master of non-conducting material shaped in accordance with the articles to be moulded, a conducting surface, depositing nickel alloy on said conducting surface in an electrolytic bath consisting essentially in each gallon of aqueous solution of 33 to 50 ozs. of nickel sulphate, 4 to 6 ozs. of boric acid, 1 to 2½ ozs. of sodium fluoride, 1 to 3½ ozs. of cobalt sulphate, ¼ to 2 ozs. of sodium chloride, 4 to 20 grams of an organic hardener and stress reliever having a sodium naphthalene trisulphonate base, and 4 to 12 grams of a wetting agent consisting of a sulphonated aliphatic alcohol, removing the master from the bath when the deposit has reached a desired thickness and detaching the deposit to thereby secure and form the mould.

4. A process for producing the surface of a pressure mould of nickel cobalt alloy which consists of providing on a master of non-conducting material shaped in accordance with the articles to be moulded, a conducting surface, depositing nickel alloy on said conducting surface in an electrolytic bath consisting essentially in each gallon of aqueous solution of 33 to 50 ozs. of nickel sulphate, 4 to 6 ozs. of boric acid, 1 to 2½ ozs. of sodium fluoride, 1 to 3½ ozs. of cobalt sulphate, ¼ to 2 ozs. of sodium chloride, 4 to 20 grams of an organic hardener and stress reliever having a sodium naphthalene trisulphonate base, 4 to 12 grams of a wetting agent consisting of a sulphonated aliphatic alcohol, and 0.2 to 1 gram of cadmium oxide, removing the master from the bath when the deposit has reached a desired thickness and detaching the deposit to thereby secure and form the mould.

5. A process for producing the surface of a pressure mould of nickel cobalt alloy which consists of providing on a master of non-conducting material shaped in accordance with the articles to be moulded, a conducting surface, depositing nickel alloy on said conducting surface in an electrolytic bath consisting essentially in each gallon of aqueous solution of 33 to 50 ozs. of nickel sulphate, 4 to 6 ozs. of boric acid, 1 to 2½ ozs. of sodium fluoride, 1 to 3½ ozs. of cobalt sulphate,

$\frac{1}{4}$ to 2 ozs. of sodium chloride, 4 to 20 grams of an organic hardener and stress reliever having a sodium naphthalene trisulphonate base, and 4 to 12 grams of a wetting agent consisting of a sulphonated aliphatic alcohol, at a current density of 8-25 amperes per square foot, removing the master from the bath when the deposit has reached a desired thickness and detaching the deposit to thereby secure and form the mould.

6. A process for producing the surface of a pressure mould of nickel cobalt alloy which consists of providing on a master of non-conducting material shaped in accordance with the articles to be moulded, a conducting surface, depositing nickel alloy on said conducting surface in an electrolytic bath consisting essentially in each gallon of aqueous solution of 33 to 50 ozs. of nickel sulphate, 4 to 6 ozs. of boric acid, 1 to $2\frac{1}{2}$ ozs. of sodium fluoride, 1 to $3\frac{1}{2}$ ozs. of cobalt sulphate, $\frac{1}{4}$ to 2 ozs. of sodium chloride, 4 to 20 grams of an organic hardener and stress reliever having a sodium naphthalene trisulphonate base, and 4 to 12 grams of a wetting agent consisting of a sulphonated aliphatic alcohol, at a current density of 8-25 amperes per square foot and at a temperature of 35 to 45° C., removing the master from the bath when the deposit has reached a desired thickness and detaching the deposit to thereby secure and form the mould.

PETER SPIRO.

FRITZ WOHLGEMUTH.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
998,085	Gibbs	July 18, 1911
2,119,304	Viers et al.	May 31, 1938
2,125,229	Harshaw et al.	July 26, 1938
2,147,415	Tucker	Feb. 14, 1939
2,191,813	Brown	Feb. 27, 1940
2,198,267	Lind et al.	Apr. 23, 1940
2,228,991	Freed	Jan. 14, 1941
2,238,861	Lind et al.	Apr. 15, 1941
2,313,756	Loose	Mar. 16, 1943
2,315,802	Lind	Apr. 6, 1943

FOREIGN PATENTS

Number	Country	Date
438,412	Great Britain	Nov. 15, 1935

OTHER REFERENCES

- Industrial and Engineering Chemistry, vol. 33, No. 12, pp. 1546-1548, December 1941.
- 25 Metal Industry (London), pp. 299, 300, May 11, 1945.
- Metal Finishing, June 1940, pp. 318-320 (an article by Weisberg).
- Meals Handbook, A. S. M., 1939 edition, pp. 1628, 1629.
- 30