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(54) ELECTROLESS NICKEL POLYALLOYS AND PLATING BATHS THEREFOR

(71) We, RICHARDSON CHEMICAL COMPANY, a corporation of Delaware, 2400 East Devon Avenue, Des Plaines, Illinois, United States of America, 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 nickel polymetallic alloys deposited electrolessly and in particular to such nickel alloys including either boron or phosphorus and one or more metals selected from tin, copper, molybdenum and tungsten. The present invention also relates to electroless plating baths for producing such alloys.

Nickel alloys achieved by electroless plating techniques have been produced in electroless plating baths, where the plating is conducted without the application of an external electrical current, utilizing a variety of different plating systems. Production of such alloys containing boron or phosphorus have heretofore been achieved by known procedures involving primarily the employment of reducing agents for the nickel cation in the bath such as nitrogen compounds to produce the boron containing alloys and phosphite ion generators to produce the phosphorus containing alloys. Formation of such electroless nickel-boron or nickel-phosphorus alloys containing other codeposited metals such as tin, tungsten, molybdenum and/or copper have, however, heretofore been either difficult or impossible to achieve when employing these conventional plating systems and techniques.

It has now been discovered that such polymetallic alloys of nickel can be more readily achieved and moreover some of the alloy deposits produced have highly desirable properties including corrosion resistance and freedom from ferromagnetism. These polymetallic alloys moreover can be produced with substantial amounts of the codeposited metals, such as tungsten, within the alloys at levels not heretofore obtainable.

These results can be achieved, in accordance with the present invention, through the employment of an ester complex of an oxyacid and a polyhydric compound in the electroless plating bath which both facilitates and permits the formation of the polymetallic alloy and, in certain instances, can also conveniently serve as the source of the metal codeposited with the nickel. In addition employment of such an ester complex can allow the electroless plating to be conducted free of the previous plating limitations such as restrictive pH ranges or highly alkaline conditions which render utilization of such an ester complex in electroless nickel plating of a particular commercial desirability.

According to the present invention there is provided an aqueous plating bath for electrolessly depositing a polymetallic nickel alloy containing nickel and either boron or phosphorus and at least one metal selected from tin, tungsten, molybdenum and copper, such bath including a source of nickel metal cation; a source of at least one metal cation selected from tin, tungsten, molybdenum and copper; a reducing agent which is either a boron containing compound or a source of hydrophosphite ion; and an ester complex of an oxyacid and a polyhydric compound (wherein the oxyacid may be the said source of molybdenum or tungsten).

The ester complex of the polyhydric compound employed in the bath is preferably an ester formed between an oxyacid and a polyhydric acid or alcohol. The polyhydric acids or alcohols which may be employed for such purpose are preferably carboxylic acids or alcohols which contain at least two hydroxy groups and from about three to about fifteen carbon atoms per molecule. Typical polyhydric compounds include acids such as tartaric, gluconic or glucoheptonic or alcohols such as mannitol, 2,3-butanediol or 1,2,3-propanetriol. Of these various polyhydric compounds, however, the carboxylic acids are generally preferred and a particular suitable polyhydric acid is glucoheptonic acid.

The oxyacids which may be reacted with the polyhydric compounds to form the ester complex are generally inorganic acids of such metals and non-metals as boron, tungsten, molybdenum, chromium or arsenic which form oxyacids such as boric, tungstic, molybdic or chromic acids. Of the various oxyacids, however, which may be employed the tungstic, molybdic and boric acids are particularly preferred especially when they are esterified with the preferred polyhydric acids such as glucoheptonic acid to form highly preferred and suitable ester complexes such as the boron, molybdenum or tungsten esters of glucoheptonic acid.

The ester complexes may also and in certain instances preferably are in the form of a polyester, that is an ester complex formed by reacting two or more mols of the oxyacid with one mol of the polyhydric compound. A typical example of such polyester and also illustrative of a particularly preferred ester complex is the diboron ester of glucoheptonic acid formed by reacting two mols of boric acid with one mol of glucoheptonic acid.

The ester complex can be prepared employing conventional techniques which basically involve reacting the desired oxyacid with the desired polyhydric compound under suitable esterification conditions and thereafter recovering the ester complex. As formed and generally in aqueous solution, the ester complex is believed to exist as a complex equilibrium mixture where the cation of the oxyacid such as boron of boric acid forms one or more ester linkages either with two hydroxyl groups of the polyhydric compound or with one hydroxy group and one carboxylic acid group when the polyhydric compound is an acid such as glucoheptonic acid. The ester complex so prepared, in addition to promoting the codeposition of the other metals with nickel, also favourably influences the rate of metal deposition and moreover is stable in the electroless plating bath thus permitting its use over long plating periods.

The production of the electroless nickel polymetallic alloys utilizing an ester complex of an oxyacid and a polyhydric compound in an electroless plating bath can, in general, be conducted according to the procedures conventionally employed for electroless nickel plating. Such procedure basically involves the formation of an aqueous electroless plating bath by adding the desired components to the bath and thereafter inserting a suitable substrate into the bath and permitting the polymetallic nickel alloy to deposit or plate upon such substrate while maintaining the desired plating conditions. If necessary a pH regulator is included in the bath.

When tungsten or molybdenum is desired as the metal for codeposition with nickel instead of simply adding a source of tungsten or molybdenum cation to the bath, for example a tungsten or molybdenum salt, the source of the tungsten or molybdenum, in accordance with a preferred embodiment, may conveniently be the complex ester itself. Normally the ester complex of the polyhydric compound does not enter into or become a component of the final polymetallic alloy. However, when the ester complex is a tungsten or a molybdenum ester, for example the tungsten or molybdenum ester of glucoheptonic acid, then the ester can also serve conveniently as the source of the tungsten or molybdenum codeposited with nickel in the final polyalloy.

As previously discussed the reducing agent for the nickel cation in the bath may be either a boron compound such as an amine borane or a phosphate ion

generator such as sodium hypophosphite which, respectively, additionally serves in accordance with known procedures as the source of the desired boron or phosphorus element within the polymetallic alloy. The boron reducing agent is, of course, employed when boron is desired and the phosphate generator employed when phosphorus is desired. The boron containing compounds which may be employed for such purposes include any of those boron containing compounds conventionally employed in electroless nickel plating as reducing agents. Typical examples of such boron containing compounds include boron hydrides, amine boranes or lower alkyl substituted amine boranes such as dimethyl- or diethyl amine borane. Generally, however, of the various boron compounds which may be employed the alkylamine boranes, and particularly dimethylamine borane are preferred for use in the electroless nickel bath particularly when utilizing such preferred ester complexes as the diboron ester of glucoheptonic acid.

The source of the nickel cations as well as the sources of the metal cations of tin and copper, when desired, in any particular bath may include any of the water soluble or semi-soluble salts of such metals which are conventionally employed for such plating. Of these metal salts, sources of the nickel cations may, for example, include nickel chloride, nickel sulfamate or nickel sulfate. Suitable salts as the source of the tin cations may include stannous chloride or stannous floroborate and suitable salts as the source of the copper cations may include both cupric and cuprous salts such as cuprous chloride or sulfate.

In operating the electroless plating bath to prepare the polymetallic nickel alloys typically an aqueous bath is first prepared by adding the bath components such as the ester complex, reducing agent and sources of the nickel cations and other desired metal cations and a pH regulator to adjust the pH followed by immersion of a suitable substrate within the bath so prepared upon which the polymetallic alloy is to be plated or deposited. The substrate employed for such purpose may be a metal such as aluminium or mild steel or a non-metal such as a plastic. When such substrate is a non-metal, however, the non-metal should in accordance with established procedures be surface activated so as to permit the deposit to form thereon.

The desired composition of the polyalloy is, of course, controlled by the selection of the desired components added to the bath. For example, as previously discussed for the nickel polyalloy to contain the chosen elements of phosphorus or boron then either a phosphorus or boron reducing agent is employed respectively. Also if, in addition to nickel, tin or copper or both are desired in the polyalloy then a suitable source or sources of either or both the metal cations of tin or copper will be added to the bath in addition to the source of nickel cation. Moreover, if tungsten or molybdenum is desired as a component either codeposited with the nickel alone or codeposited with nickel, tin and copper then the ester complex employed in the bath will, as previously discussed, preferably be an ester of tungsten or molybdenum such as the tungsten or molybdenum ester of glucoheptonic acid.

The conditions employed in conducting the plating will be dependent upon the desired final concentration of the metal or metals codeposited with nickel in the polyalloy, the various bath components and the reducing agent employed as well as the quantity of phosphorus or boron desired in the polyalloy. Moreover the final composition of the alloy and particularly the quantity of the metals codeposited with nickel will be a function of the pH range, concentration of the metal cation and temperatures of the bath. Accordingly the conditions as described hereinafter may be varied somewhat within the indicated ranges to achieve a variety of different alloy compositions.

The concentration of the metal cations maintained within the bath may be varied but generally sufficient sources of the metal cations are added to maintain the concentration of the metal cations within certain preferred ranges. For example, a source of nickel cation should be added to the bath sufficient to provide a concentration of nickel cation of from 0.05 to 0.3 mols per liter. When tin and/or copper are desired in the polyalloy a source of copper cations should be added sufficient to provide a concentration of cuprous or cupric cation within the range of from 0.0005 to 0.01 mols per liter and/or a source of stannous or stannic ion sufficient to provide a tin cation concentration of from 0.01 to 0.1 mols per liter.

The concentration of the ester complex maintained within the bath may also be varied with the amount chosen for any particular bath being a function of the specific ester complex employed as well as the particular polyalloy desired.

Generally, however, when employing the preferred ester complexes such as the boron molybdenum or tungsten esters of glucoheptonic acid, the amount utilized will generally range from 0.0005 to 1.0 mols per liter with a more limited range of from 0.001 to 0.5 mols per liter being generally preferred in most instances.

The pH employed for the bath solution will affect the final composition of the polyalloy in terms of the quantity of metals codeposited as well as the amount of boron or phosphorus present. For example in conducting a bath for the preparation of a nickel-boron-tungsten alloy when the pH is maintained at about 9.6 a substantial quantity of tungsten is codeposited with nickel in the order of 20 weight percent. When, however, the pH is lower and within the range of about 5.9 the quantity of tungsten is reduced to about 12 weight percent of the alloy. When employing an ester complex, such as the diboron ester of glucoheptonic acid, the electroless bath may be operated over the rather wide pH range of from four to fourteen. This is somewhat surprising in that the prior art baths for producing nickel alloys generally had to be operated at relatively high pH ranges or within narrow and critical pH ranges in order to obtain any substantial level of metal codeposited with nickel. This versatile pH range, moreover, can free operation of the present bath from any critical pH control, thus permitting the bath to be operated in a relatively simple and commercially desirable manner. The particular pH range desired for the bath may, of course, be readily controlled in accordance with conventional procedures by adding a suitable quantity of an acid or base as a pH regulator to adjust the pH for the plating of any specific polymetallic alloy.

The quantity of the boron or phosphite reducing agent present in the bath will normally be at least sufficient to reduce the nickel cation to free metal. Typically the concentration of the boron containing compounds in the bath such as dimethyl amine borane will range from 0.01 to 0.3 mols and the concentration of the phosphite ion generator such as sodium hypophosphite will range from 0.05 to 1 mols per liter.

The temperature at which the plating bath is maintained is, in part, a function of the desired rate of plating as well as the composition of the bath and in particular depends upon whether a phosphite or boron reducing agent is employed. Typically, however, the temperature may range from about 25°C to substantially boiling or 100°C, with the temperature within such range usually being lower when using the boron reducing agents and higher when using the phosphite reducing agent but in general a bath temperature of from 60 to 90°C. is satisfactory under most circumstances.

The duration of the plating will depend upon such factors as the quantity of alloy desired as a plating deposit upon the particular substrate as well as the composition of the bath. Generally, however, when utilizing the ester complexes relatively high plating rates can be achieved in the order of from about 2.5 to 75 microns per hour. Accordingly the duration of any plating will be adjusted to achieve the desired level of deposit based upon such deposition rates.

The plating bath may, if desired, contain conventional bath additives which are commonly employed in electroless nickel plating baths. Included within such conventional materials are bath stabilizers such as sulfur containing compounds, for example thiourea, as well as complexing agents for the metal ions maintained within the bath such as ethylene diamine tetra acetic acid (EDTA), potassium pyrophosphate or polyamines or sulfide ion controllers such as lead.

The present invention also extends to a polymetallic nickel alloy deposited electrolessly from a bath according to this invention wherein the alloy includes nickel and either phosphorus or boron and at least one metal selected from tin, tungsten, molybdenum and copper. The polymetallic nickel alloys obtained include nickel as the principle component. Typical examples of the polymetallic nickel alloys which may be produced include nickel polyalloys containing phosphorus such as nickel-phosphorus-tin; nickel-phosphorus-tungsten; nickel-phosphorus-molybdenum; nickel-phosphorus-copper; nickel-phosphorus-molybdenum-copper; nickel-phosphorus-tin-tungsten; or nickel-phosphorus-tin-copper; and nickel alloys containing boron such as nickel-boron-tin; nickel-boron-tungsten; nickel-boron-copper; nickel-boron-tin-tungsten; nickel-boron-molybdenum; nickel-boron-molybdenum-copper; or nickel-boron-tin-copper. Generally, these polyalloys are characterised as having good corrosion resistance of an order superior to conventional nickel-phosphorus or nickel-boron alloys and provide, for example, excellent corrosion protection for various metal substrates such as mild steel or aluminium.

The polyalloys are composed primarily of nickel and generally in the range of

from 60 to 95 weight percent of the alloy. The other components of the alloy will, of course, vary in respect to the other metals codeposited with nickel and the boron or phosphorus element present as well as the quantity of such metals or elements present in the poly-alloy. Basically, however, the alloy may include tin within the range of from 0.2 to 10 weight percent; tungsten within the range of from 0.1 to 25 weight percent; copper within the range of from 0.1 to 39 weight percent; molybdenum within the range of from 0.1 to 27 weight percent; phosphorus within the range of from 4 to 20 weight percent and boron within the range of from 0.02 to 5 weight percent.

The polymetallic nickel alloys are characterised by a number of desirable physical, mechanical and electromagnetic characteristics. While the specific properties for any particular polyalloy within this class will, of course, vary depending upon its particular composition as well as upon the composition of the bath from which it is prepared, the polyalloys in general have excellent mechanical and corrosion resistant properties which render them of particular value in a number of commercial applications and especially in corrosive environments. Moreover, certain of these polyalloys, for example the phosphorus containing nickel alloys and specifically the nickel-phosphorus-tin-copper alloys, exhibit a nonmagnetic or non-ferromagnetic property.

In addition, these alloys exhibit a favourable surface topology with the surfaces of certain of the alloys being substantially devoid of microporosity and further show, under X-ray diffractive analysis, a low order structure with a crystallite size in the order of 15 angstroms. Moreover, the polyalloys of nickel and particularly those containing copper exhibit a highly homogeneous or unitary phase as a true alloy and are substantially free of distinct metal layers such as free copper interdispersed within the polyalloy.

One of the more desirable properties exhibited by some of the polyalloys and in particular the phosphorus containing alloys such as nickel-phosphorus-tin-copper is their lack of magnetic or ferromagnetic properties. In general, alloys of nickel-phosphorus, formed by electroless plating techniques, are initially devoid of magnetic or ferromagnetic properties. However, after aging the amorphous character of the alloy as originally deposited gradually alters and the alloy assumes a more crystalline structure which then renders the alloy ferromagnetic. Quite significantly, however, the polyalloys and specifically the nickel-phosphorus-tin-copper polyalloys do not undergo such structural alteration and do not change their original amorphous character even after aging under elevated temperatures. Hence they retain their initial non-ferromagnetic properties over long periods. Such characteristic is of particular value in that it permits such polyalloys with its superior micro-hardness and corrosion resistant properties, to be employed in electromagnetic signal recording systems as a protective and supportive alloy without adversely affecting or interfering with the desired electromagnetic properties of such signal recording system.

The following Examples are described to illustrate baths and polyalloys embodying the present invention:

EXAMPLE 1.

Preparation of ester complexes of polyhydric compounds:

- A. The diboron ester of glucoheptonic acid was prepared as follows:
Approximately 124 grams (2 mols) of boric acid and 248 grams (1 mol) of sodium glucoheptonate were charged to an esterification vessel containing about 600 milliliters of water as a solvent. With stirring, the temperature was maintained at about 25°C. for approximately 30 minutes. The mixture was thereafter diluted to a final volume of one liter with additional water.
- B. The tungsten ester of glucoheptonic acid was prepared as follows:
Approximately 330 grams (1 mol) of the sodium salt of tungstic acid (sodium tungstate) and 248 grams (1 mol) of sodium glucoheptonate were charged to an esterification vessel containing about 600 ml. of water as a solvent. With stirring, the temperature was maintained at about 25°C. for approximately 30 minutes. The mixture was thereafter diluted to a final volume of one liter with additional water.
- C. The molybdenum ester of glucoheptonic acid was prepared as follows:
Approximately 241 grams (1 mol) of the sodium salt of molybdic acid (sodium molybdate) and 248 grams (1 mol) of sodium glucoheptonate were charged to an

esterification vessel containing about 600 ml. of water as a solvent. With stirring, the temperature was maintained at about 25°C. for approximately 30 minutes. The mixture was thereafter diluted to a final volume of one liter with additional water.

EXAMPLE 2.

Plating Baths

A series of electroless plating baths were formulated utilizing the ester complexes of Example 1 to prepare the baths and alloys.

The baths prepared, the bath components employed and the electroless nickel containing alloys obtained are summarised in the following Examples.

In general, each bath of the following Examples was prepared in accordance with conventional procedures employed for nickel electroless plating using stock solutions prepared for the bath components and utilizing deionized, carbon treated and filtered water and plating grade chemicals. The alloy deposits were formed on an aluminium substrate and the substrates thereafter flexed to remove the deposited alloy for analysis by spectrographic, emission and absorption techniques.

The plating deposits obtained typically ranged in thickness from about 50 to about 100 microns representing deposition rates ranging from about 2.5 to about 75 microns per hour.

EXAMPLE 3.

Nickel-Boron-Tungsten

The above alloy was prepared utilizing the following baths at the indicated conditions:

Baths	A	B
Tungsten ester of glucoheptonic acid, mols/liter	0.2	0.2
Nickel sulfate, mols/liter	0.1	0.1
Dimethylamine borane	0.06	0.06
Thiourea, p.p.m.	1	1
pH	9.6	5.9
Temperature, °C.	90	90
<u>Alloy Analysis Weight Percent</u>		
Nickel	77.4	85.6
Boron	2.6	2.1
Tungsten	20.0	12.3

EXAMPLE 4.

Nickel-Boron-Tin-Tungsten

The above alloy was prepared utilizing the following bath at the indicated conditions:

	Tungsten ester of glucoheptonic acid, mols/liter	0.2	5
	Nickel sulfate, mols/liter	0.1	
	Stannous chloride, mols/liter	0.025	
	Dimethylamine borane, mols/liter	0.06	
	Thiourea, p.p.m.	1	
10	pH	7.5	10
	Temperature, °C.	90	
	<u>Alloys Analysis Weight Percent</u>		
	Nickel	77.9	
	Boron	1.9	
15	Tin	4.2	15
	Tungsten	16.0	

EXAMPLE 5.

Nickel-Boron-Tin

The above alloy was prepared utilizing the following baths at the indicated conditions:

20	Baths	A	B	20
	Diboron ester of glucoheptonic acid, mols/liter	0.2	0.1	
	Nickel sulfate, mols/liter	0.1	0.1	
	Stannous chloride, mols/liter	0.025	0.1	
25	Dimethylamine borane, mols/liter	0.06	0.06	25
	Potassium pyrophosphate, mols/liter	—	0.2	
	Thiourea, p.p.m.	1	1	
	pH	5.5	9.7	
	Temperature, °C.	90	90	
30	<u>Analysis Weight Percent</u>			30
	Nickel	94.2	92.8	
	Boron	1.6	1.1	
	Tin	4.2	6.1	

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EXAMPLE 6.

Nickel-Phosphorus-Tin-Tungsten

The above alloy was prepared utilizing the following bath at the indicated conditions:

5	Tungsten ester of glucoheptonic acid, mols/liter	0.2	5
	Nickel sulfate, mols/liter	0.1	
	Stannous chloride, mols/liter	0.025	
	Sodium hypophosphite, mols/liter	0.28	
	Thiourea, p.p.m.	1	
10	pH	7.5	10
	Temperature, °C.	90	
	Analysis Weight Percent		
	Nickel	83.4	
	Phosphorus	13	
15	Tin	2.2	15
	Tungsten	1.4	

EXAMPLE 7.

Nickel-Phosphorus-Tin

The above alloy was prepared utilizing the following baths at the indicated conditions:

	Baths	A	B	
	Diboron ester of glucoheptonic acid, mols/liter	0.2	0.1	
	Nickel sulfate, mols/liter	0.1	0.1	
	Stannous chloride, mols/liter	0.025	0.1	
25	Sodium hypophosphite, mols/liter	0.25	0.28	25
	Potassium pyrophosphate, mols/liter	—	0.2	
	Thiourea, p.p.m.	1	1	
	pH	5.5	9.8	
	Temperature, °C.	90	90	
30	Analysis Weight Percent			30
	Nickel	87	93.14	
	Phosphorus	11.2	6.2	
	Tin	1.8	0.66	

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EXAMPLE 8.

Nickel-Phosphorus-Tin-Copper

The above alloy was prepared utilizing the following baths at the indicated conditions:

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Baths	A	B	C	D
Diboron ester of glucoheptonic acid, mols/liter	0.1	0.025	0.1	0.015
Nickel sulfate, mols/liter	0.1	0.1	0.1	0.12
Stannous chloride, mols/liter	0.1	0.01	0.01	0.025
Copper sulfate, mols/liter	0.001	0.0005	0.0005	0.001
Sodium hyphosphite, mols/liter	0.2	0.28	0.28	0.28
Potassium pyrophosphate, mols/liter	0.2	—	—	—
Thiourea, p.p.m.	1	—	—	—
Lactic acid, mols/liter	—	0.375	0.375	—
Propionic acid, mols/liter	—	0.135	0.135	—
Citric acid, mols/liter	—	0.071	0.071	—
Lead, p.p.m.	—	0.5	0.5	—
pH	10.5	5.0	4.9	5.0
Temperature, °C.	85	90	90	90
Analysis Weight Percent				
Nickel	92.51	84.19	85.3	74
Phosphorus	3.6	14.0	11.2	16
Copper	3.4	1.6	2.4	2.0
Tin	0.49	0.21	1.1	8.0

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EXAMPLE 9.

Nickel-Boron-Tin-Copper

The above alloy was prepared utilizing the following bath at the indicated conditions:

5	Diboron ester of glucoheptonic acid, mols/liter	0.025	5
	Nickel sulfate, mols/liter	0.1	
	Stannous chloride, mols/liter	0.01	
	Copper sulfate, mols/liter	0.0005	
	Dimethylamine borane	0.06	
10	Citric acid	0.25	10
	Propionic acid	0.1	
	pH	5.1	
	Temperature, °C.	75	
	<u>Analysis Weight Percent</u>		
15	Nickel	90.6	15
	Boron	1.5	
	Tin	1.6	
	Copper	6.3	

EXAMPLE 10.

Nickel-Boron-Molybdenum

The above alloy was prepared utilizing the following bath at the indicated conditions:

	Molybdenum ester of glucoheptonic acid, mols/liter	0.001	
	Nickel sulfate, mols/liter	0.1	
25	Dimethylamine borane, mols/liter	0.06	25
	Lactic acid	0.3	
	pH	10.0	
	Temperature, °C.	90	
	<u>Analysis Weight Percent</u>		
30	Nickel	79.8	30
	Boron	0.2	
	Molybdenum	20	

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EXAMPLE 11.

Nickel-Phosphorus-Molybdenum

The above alloy was prepared utilizing the following bath at the indicated conditions:

5	Molybdenum ester of glucopheptonic acid, mols/liter	0.006	5
	Nickel sulfate, mols/liter	0.1	
	Sodium hypophosphite, mols/liter	0.28	
	pH	10.0	
	Temperature, °C.	90	
10	Analysis Weight Percent		10
	Nickel	70.5	
	Phosphorus	4.5	
	Molybdenum	25.0	

EXAMPLE 12.

15 Nickel-Phosphorus-Molybdenum-Copper

The above alloy was prepared utilizing the following bath at the indicated conditions:

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	Molybdenum ester of glucoheptonic acid, mols/liter	0.006	
	Nickel sulfate, mols/liter	0.1	
20	Copper sulfate, mols/liter	0.005	20
	Sodium hypophosphite, mols/liter	0.28	
	pH	10	
	Temperature, °C.	90	
	Analysis Weight Percent		
25	Nickel	77.5	25
	Phosphorus	3.2	
	Copper	5.3	
	Molybdenum	14.0	

EXAMPLE 13.

Nickel-Boron-Molybdenum-Copper

The above alloy was prepared utilizing the following bath at the indicated conditions:

5	Molybdenum ester of glucoheptonic acid, mols/liter	0.001	5
	Nickel sulfate, mols/liter	0.1	
	Copper sulfate, mols/liter	0.0005	
	Dimethylamine borane	0.06	
	Lactic acid	0.3	
10	pH	10	10
	Temperature, °C.	90	
	Analysis Weight Percent		
	Nickel	77.87	
	Boron	0.33	
15	Molybdenum	20	15
	Copper	1.8	

WHAT WE CLAIM IS:—

1. An aqueous plating bath for electrolessly depositing a polymetallic nickel alloy containing nickel and either boron or phosphorus and at least one metal selected from tin, tungsten, molybdenum and copper, such bath including a source of nickel metal cation; a source of at least one metal cation selected from tin, tungsten, molybdenum and copper; a reducing agent which is either a boron containing compound or a source of hyphosphite ion; and an ester complex of an oxyacid and a polyhydric compound (wherein the oxyacid may be the said source of molybdenum or tungsten).

2. A bath according to claim 1 wherein the ester complex is an ester of a polyhydric acid or alcohol selected from carboxylic acids and alcohols having at least two hydroxy groups and from about 3 to 15 carbon atoms per molecule.

3. A bath according to claim 1 or claim 2 wherein the ester complex is formed by reacting an inorganic oxyacid with the polyhydric compound.

4. A bath according to any one of the preceding claims wherein the ester is formed by reacting at least two mols of the oxyacid with one mol of the polyhydric compound.

5. A bath according to any one of the preceding claims wherein the polyhydric compound is glucoheptonic acid.

6. A bath according to any one of the preceding claims wherein the complex is a boron ester.

7. A bath according to any one of claims 1 to 6 wherein the complex is a tungsten ester.

8. A bath according to any one of claims 1 to 6 wherein the complex is a molybdenum ester.

9. A bath according to claim 4, wherein the complex is the diboron ester of glucoheptonic acid.

10. A bath according to any one of the preceding claims wherein the ester complex is present within the range of from 0.0005 to 1.0 mols per liter.

11. A bath according to claim 10 wherein the ester complex is present within the range of from 0.001 to 0.5 mols per liter.

12. A bath according to any one of claims 1 to 6 wherein copper cations are present within the range of from 0.005 to 0.01 mols per liter.

(21)



EXAMPLE 13.

Nickel-Boron-Molybdenum-Copper

The above alloy was prepared utilizing the following bath at the indicated conditions:

5	Molybdenum ester of glucoheptonic acid, mols/liter	0.001	5
	Nickel sulfate, mols/liter	0.1	
	Copper sulfate, mols/liter	0.0005	
	Dimethylamine borane	0.06	
	Lactic acid	0.3	
10	pH	10	10
	Temperature, °C.	90	
	Analysis Weight Percent		
	Nickel	77.87	
	Boron	0.33	
15	Molybdenum	20	15
	Copper	1.8	

WHAT WE CLAIM IS:—

1. An aqueous plating bath for electrolessly depositing a polymetallic nickel alloy containing nickel and either boron or phosphorus and at least one metal selected from tin, tungsten, molybdenum and copper, such bath including a source of nickel metal cation; a source of at least one metal cation selected from tin, tungsten, molybdenum and copper; a reducing agent which is either a boron containing compound or a source of hyphosphite ion; and an ester complex of an oxyacid and a polyhydric compound (wherein the oxyacid may be the said source of molybdenum or tungsten).
2. A bath according to claim 1 wherein the ester complex is an ester of a polyhydric acid or alcohol selected from carboxylic acids and alcohols having at least two hydroxy groups and from about 3 to 15 carbon atoms per molecule.
3. A bath according to claim 1 or claim 2 wherein the ester complex is formed by reacting an inorganic oxyacid with the polyhydric compound.
4. A bath according to any one of the preceding claims wherein the ester is formed by reacting at least two mols of the oxyacid with one mol of the polyhydric compound.
5. A bath according to any one of the preceding claims wherein the polyhydric compound is glucoheptonic acid.
6. A bath according to any one of the preceding claims wherein the complex is a boron ester.
7. A bath according to any one of claims 1 to 6 wherein the complex is a tungsten ester.
8. A bath according to any one of claims 1 to 6 wherein the complex is a molybdenum ester.
9. A bath according to claim 4, wherein the complex is the diboron ester of glucoheptonic acid.
10. A bath according to any one of the preceding claims wherein the ester complex is present within the range of from 0.0005 to 1.0 mols per liter.
11. A bath according to claim 10 wherein the ester complex is present within the range of from 0.001 to 0.5 mols per liter.
12. A bath according to any one of claims 1 to 6 wherein copper cations are present within the range of from 0.005 to 0.01 mols per liter.



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13. A bath according to any one of claims 1 to 6 wherein tin cations are present within the range of from 0.01 to 0.1 mols per liter.

14. A bath according to any one of the preceding claims wherein the nickel cations are present within the range of from 0.05 to 0.3 mols per liter.

15. A bath according to any one of the preceding claims wherein the reducing agent is a boron-nitrogen compound.

16. A bath according to claim 15 wherein the reducing agent is dimethylamine borane.

17. A bath according to claim 15 or claim 16 wherein the boron reducing agent is present within the range of from 0.01 to 0.3 mols per liter.

18. A bath according to any one of claims 1 to 14 wherein the reducing agent is an alkali metal hypophosphite.

19. A bath according to claim 18 wherein the phosphite reducing agent is present within the range of from 0.05 to 1.0 mols per liter.

20. A bath according to any one of the preceding claims wherein the pH is in the range of from 4 to 14.

21. A bath according to any one of the preceding claims wherein the temperature is maintained within the range of from 25°C. to 100°C.

22. A bath according to claim 1 wherein the nickel alloy contains nickel, boron and tungsten, the reducing agent is dimethylamine borane and the complex is the tungsten ester of glucoheptonic acid.

23. A bath according to claim 1 wherein the alloy contains nickel, boron, tin and tungsten, the bath includes a source of tin cations, the reducing agent is dimethylamine borane and the complex is the tungsten ester of glucoheptonic acid.

24. A bath according to claim 1 wherein the alloy contains nickel, boron and tin, the bath includes a source of tin cations, the reducing agent is dimethylamine borane and the complex is the diboron ester of glucoheptonic acid.

25. A bath according to claim 1 wherein the alloy contains nickel, phosphorus, tin and tungsten, the bath includes a source of tin cations, the reducing agent is sodium hypophosphite and the complex is the tungsten ester of glucoheptonic acid.

26. A bath according to claim 1 wherein the alloy contains nickel, phosphorus and tin, the bath includes a source of tin cations, the reducing agent is sodium hypophosphite and the complex is the diboron ester of glucoheptonic acid.

27. A bath according to claim 1 wherein the alloy contains nickel, phosphorus, tin and copper, the bath includes a source of tin cations and a source of copper cations, the reducing agent is sodium hypophosphite and the complex is the diboron ester of glucoheptonic acid.

28. A bath according to claim 1 wherein the alloy contains nickel, boron, tin and copper, the bath includes a source of tin cations and a source of copper cations, the reducing agent is dimethylamine borane and the complex is the diboron ester of glucoheptonic acid.

29. A bath according to claim 1 wherein the alloy contains nickel, phosphorus, molybdenum and copper, the bath includes a source of copper cations, the reducing agent is sodium hypophosphite and the complex is the molybdenum ester of glucoheptonic acid.

30. A bath according to claim 1 wherein the alloy contains nickel, phosphorus and molybdenum, the reducing agent is sodium hypophosphite and the complex is the molybdenum ester of glucoheptonic acid.

31. A bath according to claim 1 wherein the alloy contains nickel, boron and molybdenum, the reducing agent is dimethylamine borane and the complex is the molybdenum ester of glucoheptonic acid.

32. A bath according to claim 1 wherein the alloy contains nickel, boron, molybdenum and copper, the bath includes a source of copper cations and the reducing agent is dimethylamine borane.

33. A polymetallic nickel alloy deposited electrolessly from a bath according to claim 1 wherein the alloy includes nickel and either phosphorus or boron and at least one metal selected from tin, tungsten, molybdenum and copper.

34. A polymetallic nickel alloy according to claim 33 including nickel, tin, and either phosphorus or boron.

35. An alloy according to claim 34 including tin within the range of from 0.2 to 10 weight percent, and phosphorus within the range of from 4 to 20 weight percent or boron within the range of from about 0.02 to about 5 weight percent; with the balance being nickel.

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36. An alloy according to claim 34 or claim 35 further including tungsten and/or copper.
- 5 37. An alloy according to claim 36 including tungsten within the range of from 0.1 to 25 weight percent and/or copper within the range of from 0.1 to 30 weight percent.
38. A polymetallic nickel alloy according to claim 33 including nickel, boron and tungsten.
- 10 39. An alloy according to claim 38 wherein the alloy includes boron within the range of from 0.02 to 5 weight percent and tungsten within the range of from 0.1 to 25 weight percent with the balance being nickel. 10
40. An alloy according to claim 38 including tungsten in an amount greater than 20 weight percent.
- 15 41. A polymetallic nickel alloy according to claim 33 including nickel, molybdenum and either phosphorus or boron. 15
42. An alloy according to claim 41 including molybdenum within the range of from 0.1 to 27 weight percent; and phosphorus within the range of from 4 to 20 weight percent or boron within the range of from 0.02 to 5 weight percent; with the balance being nickel. 15
- 20 43. An alloy according to claim 41 or claim 42 further including copper. 20
44. An alloy according to claim 43 including copper within the range of from 0.1 to 39 weight percent. 20
45. An alloy according to any one of claims 33 to 44 including nickel within the range of from 60 to 95 weight percent.
- 25 46. A method for the electroless depositing of a polymetallic nickel alloy comprising the step of plating a substrate in an aqueous bath according to any one of claims 1 to 32. 25
47. A method for the electroless depositing of a polymetallic nickel alloy substantially as herein described and with reference to any one of the examples 2 to 13.
- 30 48. A polymetallic nickel alloy produced by the method of claim 46 or claim 47. 30
49. A plating bath substantially as herein described and with reference to any of the Examples 2 to 13.
- 35 50. A polymetallic nickel alloy deposited electrolessly substantially as herein described and with reference to any one of the Examples 2 to 13. 35

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