

1

3,093,557

METHODS AND ELECTROLYTES FOR DEPOSITING NICKEL AND COBALT

Richard P. Cope, Jr., Wilkinsburg, and John R. Drobne, Munhall, Pa., assignors to Westinghouse Electric Corporation, East Pittsburgh, Pa., a corporation of Pennsylvania

No Drawing. Filed Aug. 25, 1961, Ser. No. 133,800
14 Claims. (Cl. 204—43)

This invention relates to bright metal electroplating methods and novel electrolyte compositions. More particularly, this invention relates to an electrolyte from which bright nickel, cobalt and alloys of nickel-cobalt may be electrodeposited.

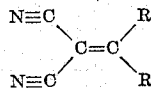
Many compounds are known to be useful as additives to nickel, cobalt and nickel-cobalt alloy electrolytes. Aliphatic nitriles are among the compounds that have been used. These nitriles have been used in conjunction with well known organic sulfon-compounds known in the art as carriers or regulators. Examples of systems incorporating nitriles in conjunction with organic sulfon-compounds as carriers or regulators are disclosed in U.S. Patent 2,882,208 and U.S. Patent 2,524,010. The known nitrile brighteners are volatile, poisonous liquids. They are extremely hazardous because they are nerve poisons that migrate through the skin, possibly effecting permanent brain damage. Not only are such compounds dangerous to handle, but many will boil out of plating baths at high temperatures. The hazards of exposure to such vapors is obvious.

Accordingly, it is the general object of this invention to provide a novel system for bright nickel plating incorporating soluble solid dicyano compounds as brighteners.

It is a more particular object of this invention to provide a system for bright nickel, cobalt and nickel-cobalt alloy plating incorporating soluble solid dicyano compounds which may be safely handled.

We have discovered a method of improving electrolytes of nickel, cobalt and nickel-cobalt alloys by the incorporation therein of a predetermined amount of a series of dicyano compounds that are solid at room temperature and are highly effective brighteners. Since they are solids, the compounds are safer to handle than the volatile nitrile liquids. While these compounds cannot be ingested without possible serious consequences, the problem of inhalation is essentially eliminated. Higher plating bath temperatures may be employed without generating hazardous vapors. Higher temperatures permit the use of higher current densities.

Using these compounds in the hereinafter described electrolytes, it is possible to electrodeposit bright coatings which are fairly ductile and level. The compounds are selected from the group consisting of dicyanoketeneethylenecetal and compounds having the formula:



wherein R is a radical selected from at least one of the group consisting of NH_2 , OR_1 and NHR_1 in which R_1 is an aliphatic monovalent hydrocarbon radical with one to three carbon atoms. The R_1 substituents need not be the same in a given compound. The brighteners of this invention may be used with sulfur-containing carriers or regulators known in the art. The aliphatic monovalent hydrocarbon radical R_1 is limited to those radicals having from one to three carbon atoms. Radicals with a greater number of carbon atoms ordinarily result in compounds that are relatively insoluble in the electrolyte. It is ap-

2

parent, then, that all solid dicyanoketene compounds cannot be satisfactorily employed in the invention.

The following series of compounds used in Examples I to IV hereinafter was produced as indicated:

(a) The dicyanoketeneethylenecetal used in Example I was prepared as follows:

12.89 grams of tetracyanoethylene, two grams of urea as a catalyst, and 24 ml. of ethylene glycol were heated on a steam bath until the tetracyanoethylene went into solution. The product was poured into 100 ml. of ice water, filtered and recrystallized in an alcohol-water solution. The resulting fluffy light brown needles had a melting point of $112-113^\circ\text{C}$.

(b) The 1,1-dicyano-2,2-diaminoethylene used in Example II was prepared as follows:

6.7 grams of dicyanoketeneethylenecetal and 21.5 ml. of concentrated ammonia were refluxed for ten minutes. The product was permitted to stand overnight. The light brown material recovered had a melting point of $247-253^\circ\text{C}$.

(c) The 1,1-dicyano-2,2-diethoxyethylene used in Example III was prepared as follows:

6.4 grams of tetracyanoethylene, 3 grams of urea as a catalyst and 50 ml. of alcohol were heated on a steam bath for 20 minutes. The product was cooled and then evaporated to 25 ml. at room temperature by blowing air across it. Then, 25 ml. of water was added. The material was cooled, filtered and air dried. The white crystals produced had a melting point of 54 to 56°C .

(d) The 1,1-dicyano-2,2-di-n-propylamine used in Example IV was prepared as follows:

6.7 grams of dicyanoketeneethylenecetal dissolved in 50 ml. of water and 10 ml. of n-propylamine were refluxed for 20 minutes. The product was cooled to 0°C . and then filtered. A light brown precipitate resulted.

The foregoing compounds are incorporated into plating baths as illustrated by the following specific examples:

Example I

40	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----oz./gal.	40
	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----oz./gal.	6
	H_3BO_3 -----oz./gal.	5
	Dicyanoketeneethylenecetal -----oz./gal.	0.05
	Saccharin -----oz./gal.	0.10
45	pH -----	2.1
	Temperature ----- $^\circ\text{F}$	140

The bath is agitated with air. A highly bright, leveled and fairly ductile nickel deposit is obtained. The deposit is bright in the current density range from 10 to 250 amps./sq. ft.

Example II

40	Cobalt sulfate, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ -----oz./gal.	67
	Sodium chloride, NaCl -----oz./gal.	2
	Boric acid -----oz./gal.	6
45	1,1-dicyano-2,2-diaminoethylene -----oz./gal.	.01
	Napthalene trisulfonic acid -----oz./gal.	1
	Sodium 2-ethylhexyl sulfate -----oz./gal.	0.003
	pH -----	4.5
60	Temperature ----- $^\circ\text{F}$	120

Agitation is achieved with cathode rod movement. A bright leveled and fairly ductile deposit is obtained. The deposit is bright in the current density range from 10 to 200 amps./sq. ft.

Example III

65	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----oz./gal.	10-30
	H_3BO_3 -----oz./gal.	0-8
	1,1-dicyano-2,2-diethoxyethylene -----oz./gal.	0.01
	Sodium styrene sulfonate -----oz./gal.	0.01
70	Sodium lauryl sulfate -----oz./gal.	0.02
	pH -----	3.5
	Temperature ----- $^\circ\text{F}$	160

Agitation is achieved with cathode rod movement. A bright, leveled and ductile nickel deposit is obtained. The deposit is bright in the current density range of from 10 to 150 amps./sq. ft.

Example IV

NiSO ₄ ·6H ₂ O	oz./gal.	32
NiCl ₂ ·6H ₂ O	oz./gal.	4
CoSO ₄ ·7H ₂ O	oz./gal.	0.4
H ₃ BO ₃	oz./gal.	4
(NH ₄) ₂ SO ₄	oz./gal.	0.1
Nickel formate	oz./gal.	6.0
1,1-dicyano-2,2-n-propylaminoethylene	oz./gal.	0.001
8-acetamido-3,6-naphthalene disulfonate	oz./gal.	2.0
pH		4.0
Temperature	° F	150

The bath is agitated with air. A bright nickel cobalt alloy deposit is obtained. The deposit is bright in the current density range of from 10 to 100 amps./sq. ft. In a similar way dimethoxy and dipropoxy compounds may be employed in the bath to replace the 1,1-dicyano-2,2-diethoxyethylene.

The chloride of the electrolyte can be added as sodium chloride or magnesium chloride. The sodium lauryl sulfate and sodium 2-ethyl hexyl sulfate are well known wetting agents. Other wetting agents, known in the art, may also be used in the baths.

The brightener components of this invention may also be incorporated into sulfamate and fluoroborate plating baths, as well as those in the examples, with equally good results. Bright plate may be obtained with brightener compounds of this invention at concentrations in the range of from 0.0005 to 0.05 oz./gal., in any of the foregoing experimental electrolytes.

Nickel-containing electrolytes suitable for electroplating nickel may be any acidic nickel salt solutions employed in the art for plating. It has been found that the single or double nickel sulfate and nickel chloride salts alone or in any combination may be employed. Other platable nickel salts may be employed. The nickel plating baths are acidic, having a pH of from 0.5 to 6. In many cases buffers, such as boric acid, and other addition agents, may be present; in some cases marked beneficial results are obtained when they are present. Examples of suitable addition agents are organic sulfonates, such as naphthalene-1,5-disulfonic acid, ammonium sulfate, formaldehyde, nickel formate, sodium sulfate, sodium lauryl sulfate, and ammonium chloride. Gum arabic and gum tragacanth and the like may be present. If required, additions of hydrochloric or sulfuric acid may be made to the electrolytes.

For plating cobalt, the electrolyte may contain cobalt sulfate, cobalt chloride or mixtures thereof. Similar addition agents to those used with nickel electrolytes may be added to these solutions to advantage. The pH of the aqueous electrolytes may be from 0.5 to 6.

In plating nickel-cobalt alloys, mixtures of nickel salts and cobalt salts are dissolved in the aqueous electrolyte. The baths have a pH range of from 0.5 to 6. For alloy plating cobalt-nickel anodes are used. Particularly useful alloys are those containing from 80% to 97% nickel by weight and 20% to 3% cobalt by weight. However, alloys containing greater amounts of cobalt may be readily plated. Alloys of nickel and/or cobalt and iron and iron alone may also be deposited from electrolytes containing the additives described heretofore with similar advantage.

The compounds of this invention are particularly valuable in fast cycle reverse current plating baths. Lower concentrations of the brighteners may be used in the fast cycle reverse current processes with excellent results. A desirable periodic reverse current process is described in U.S. Patent No. 2,470,775 to Jernstedt et al., assigned to the assignee of the instant application. A periodic reverse current in which the cathodic portion

of the cycle, applied to the member being plated with nickel, is two seconds or less or, preferably, less than one-half second and an anodic portion of the cycle from one-half to one-twenty fifth of the cathodic portion with the current densities adjusted so that the anodic portion of the cycle applies from 4% to 60% of the coulombs of current applied during the cathodic portion of the cycle, will produce excellent electrodeposits. The cycles may be reduced in time to as little as $\frac{1}{100}$ of a second cathodic period and $\frac{1}{500}$ of a second anodic period with benefit. Below an anodic time period of about $\frac{1}{500}$ second, the deplating is not effective enough to give the full advantage of periodic reverse current plating.

The following examples illustrate the results obtained with the brightener compositions of this invention in the periodic reverse current process:

Example V

NiSO ₄ ·6H ₂ O	oz./gal.	40.0
NiCl ₂ ·6H ₂ O	oz./gal.	6.5
H ₃ BO ₃	oz./gal.	5.0
Dicyanoketeneethyleneacetal	oz./gal.	0.0001
pH		3.8
Temperature	° F	140

A periodic reverse current cycle is used with periods of $\frac{1}{5}$ second and $\frac{1}{25}$ second for the cathodic and anodic portions, respectively. Bright ductile and leveled electrodeposits of nickel are obtained at from 10 to 200 amps./sq. ft.

Example VI

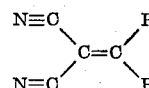
CoSO ₄ ·7H ₂ O	oz./gal.	67
NaCl	oz./gal.	2
H ₃ BO ₃	oz./gal.	6
1,1-dicyano-2,2-diaminoethylene	oz./gal.	0.0001
Saccharin	oz./gal.	0.001
pH		4.8
Temperature	° F	140

A periodic reverse current cycle is used with periods of $\frac{1}{50}$ second and $\frac{1}{100}$ second for the cathodic and anodic portions, respectively. Bright, ductile and leveled electrodeposits of cobalt are obtained from about 10 to 60 amps./sq. ft.

In the periodic reverse current processes, excellent bright deposits of nickel, cobalt and nickel-cobalt alloys can be produced from solutions having brightener compounds of this invention at concentrations as low as 0.00005 oz./gal. and as high as 0.05 oz./gal. The regular uninterrupted current processes employ the compounds at concentrations from 0.0005 to 0.05 oz./gal., as outlined heretofore. The economies of such low brightener concentrations in the periodic reverse current processes are obvious.

While there have been shown and described what are presently considered to be the preferred embodiments of the invention, modifications thereto will readily occur to those skilled in the art. It is not desired, therefore, that the invention be limited to the specific arrangements shown and described and it is intended to cover in the appended claims all such modifications as fall within the true spirit and scope of the invention. We claim as our invention:

1. An acidic solution for electrodepositing a metal selected from the group consisting of nickel, cobalt and nickel-cobalt alloys containing a soluble salt of said metal and a brightener compound selected from the group consisting of dicyanoketene-ethyleneacetal and compounds having the formula:



wherein R is selected from the group consisting of OR₁, NH₂ and NHR₁, wherein R₁ is an aliphatic monovalent hydrocarbon radical with 1 to 3 carbon atoms, said bright-

5

ener being present in a concentration range of from 0.00005 oz./gal. to 0.05 oz./gal. of solution.

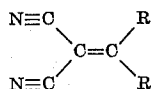
2. An acidic solution for electrodepositing a metal selected from the group consisting of nickel, cobalt and nickel-cobalt alloys containing a soluble salt of said metal and dicyanoketeneethylenecetal in a concentration range from 0.00005 to 0.05 oz./gal. of solution.

3. An acidic solution for electrodepositing a metal selected from the group consisting of nickel, cobalt and nickel-cobalt alloys containing a soluble salt of said metal and 1,1-dicyano 2,2-diaminoethylene in a concentration range from 0.00005 to 0.05 oz./gal. of solution.

4. An acidic solution for electrodepositing a metal selected from the group consisting of nickel, cobalt and nickel-cobalt alloys containing a soluble salt of said metal and 1,1-dicyano-2,2-ethoxyethylene in a concentration range from 0.00005 to 0.05 oz./gal. of solution.

5. An acidic solution for electrodepositing a metal selected from the group consisting of nickel, cobalt and nickel-cobalt alloys containing a soluble salt of said metal and 1,1-dicyano-2,2-n-propylaminoethylene in a concentration range from 0.00005 to 0.05 oz./gal. of solution.

6. A method of electrodepositing a metal selected from the group consisting of nickel, cobalt and nickel-cobalt alloys comprising the steps of electrolyzing an acidic electrolyte of said metal containing a brightener compound selected from the group consisting of dicyano-keteneethylenecetal and compounds having the formula:



wherein R is selected from the group consisting of NH_2 , OR_1 and NHR_1 wherein R_1 is an aliphatic monovalent hydrocarbon radical with 1 to 3 carbon atoms, said brightener compound being present in a concentration range from 0.00005 to 0.05 oz./gal. of solution.

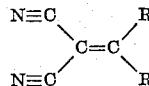
7. A method in accordance with claim 6, wherein said brightener compound is dicyanoketeneethylenecetal.

8. A method in accordance with claim 6, wherein said brightener compound is 1,1-dicyano-2,2-diaminoethylene.

9. A method in accordance with claim 6, wherein said brightener compound is 1,1-dicyano-2,2-n-propylaminoethylene.

6

10. A method of electrodepositing a metal selected from the group consisting of nickel, cobalt and nickel-cobalt alloys on a member comprising the steps of applying current to the member, while in contact with an acidic electrolyte of said metal containing a brightener compound selected from the group consisting of dicyanoketeneethylenecetal and compounds having the formula:



wherein R is selected from the group consisting of NH_2 , OR_1 and NHR_1 , wherein R_1 is an aliphatic monovalent hydrocarbon radical with 1 to 3 carbon atoms, said brightener compound being present in a concentration range from 0.00005 to 0.05 oz./gal. of solution, said current being periodically reversed so that the member is successively cathodic for a period less than two seconds, then anodic for a period $\frac{1}{2}$ to $\frac{1}{25}$ of the cathodic period but not less than $\frac{1}{600}$ of a second.

11. A method in accordance with claim 10, wherein said brightener compound is dicyanoketeneethylenecetal.

12. A method in accordance with claim 10, wherein said brightener compound is 1,1-dicyano-2,2-diaminoethylene.

13. A method in accordance with claim 10 wherein said brightener compound is 1,1-dicyano-2,2-ethoxyethylene.

14. A method in accordance with claim 10, wherein said brightener compound is 1,1-dicyano-2,2-n-propylaminoethylene.

References Cited in the file of this patent

UNITED STATES PATENTS

2,470,775	Jernstedt et al.	May 24, 1949
2,524,010	Du Rose et al.	Sept. 26, 1950
2,781,306	Brown	Feb. 12, 1957
2,882,208	Becking et al.	Apr. 14, 1959
2,972,571	Towle	Feb. 21, 1961
2,978,391	Du Rose	Apr. 4, 1961

OTHER REFERENCES

Middleton et al.: J. Am. Chem. Soc., vol. 80, pp. 2788-2795, June 1958.