United States Patent Office 2,782,153 Patented Feb. 19, 1957

2,782,153

NICKEL ELECTRODEPOSITION

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No Drawing. Application February 16, 1954, Serial No. 410,713

9 Claims. (Cl. 204—49)

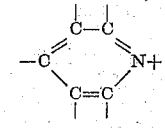
This invention relates to electrodeposition of nickel and more specifically to a process for producing electrodeposits of greatly increased brightness and smoothness, as taken from the plating solution, without buffing or polishing of any sort.

This application is a continuation-in-part of our copending application, serial No. 278,957, filed March 27, 1952, and our copending application, serial No. 338,560, filed February 24, 1953, which was a continuation-in-part of application serial No. 278,958, filed March 27, 1952, all now abandoned.

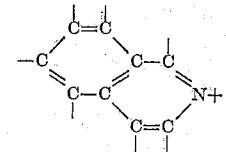
This invention is primarily concerned with the fact that although electrodeposits taken from acid nickel plating solutions containing coumarin exhibit extraordinary smoothness they are only semi-bright, and attempts to increase their brightness by the use of addition agents of the type of saccharin or naphthalene sulfonic acids result in improved brightness with loss of smoothness when the surface being coated is quite smooth, and can result in decrease in both smoothness and brightness when the surface to be coated is quite rough. It was found, for example, that when a aqueous, acid solution containing 240 grams per liter of nickel sulfate heptahydrate, 40 grams per liter of nickel chloride hexahydrate and 40 grams per liter of boric acid was utilized and coumarin was used in concentration of 0.25 gram per liter as the sole addition agent, a semi-bright deposit was obtained having a smoothness increase over the base metal of approximately 4 microinches where the base metal had a smoothness in the order of 6 to 10 microinches, measurements having been made with the Brush surface analyzer. Such an increase in smoothness is remarkable, and this property of coumarin has formed the basis of a commercial semi-bright solution now being widely used. When the attempt was made to increase the brightness by the addition of agents such as saccharin of naphthalene sulfonic acids, it was found that increased brightness was secured, but at the cost of a part of the smoothing action of the coumarin. For example, it was found that when the above described solution was varied by adding 3.5 grams per liter of naphthalene disulfonic acid an increase in brightness was secured, but the gain in smoothness over the base metal was only about 2.2 microinches, the same type of base metal being used. If, instead of using naphthalene sulfonic acids, saccharin was used to improve the brightness, improved brightness was obtained and the gain in smoothness was about the same. Many other sulfonic acids and sulfonamides show similar results. When the surface to be coated is not so smooth, e. g. 20 to 29 R. M. S. as shown by the Brush surface analyzer the loss of the smoothing action may be so great as to overshadow the tendency toward increased brightness and actually appear to decrease the luster of the deposit.

In accordance with the present invention it has now been discovered that a large portion of the lost smoothing action just described can be restored if there is added, in addition to the coumarin, not only an aromatic sulfonamide, but also one or more of certain organic, leveling addition agents of the following class:

Quaternary nitrogen compounds containing the



grouping and at least one aliphatic carbon atom attached to the nitrogen of said group. This group may be substituted to form a double ring structure of the form



(quinolinium) and one or more hydrogen atoms may be replaced by methyl or ethyl or other substituents. Preferably the compound may be of the bis-pyridinium or bis-isoquinolinium type joined by a carbon or carbon and oxygen chain such as $(CH_2)_n$ or $(CH_2)_nO(CH_2)_n$.

As examples may be mentioned,

(*a*) N,N'-(oxydiethylene)-bis isoquinolinium salts
(*b*) N,N'-(oxydiethylene)-bis pyridinium salts
(*c*) N-carboxymethyl pyridinium salts
(*d*) N,N'-(oxydimethylene)-bis-pyridinium salts
(*e*) Quinaldine methyl sulfate
(*f*) p-Xylylene pyridinium salts
(*g*) N-(2-chloroallyl) pyridinium salts
(*h*) N-methallyl pyridinium salts
(*i*) N,N'-methylene-bis-pyridinium salts
(*j*) N-(carboxy isobutyl) pyridinium salts.

While these leveling agents do not completely restore the full smoothing action of coumarin, they do, in some instances restore a large portion of it.

The preferred acid nickel solution in connection with which the invention may be realized is an aqueous solution containing nickel sulfate equivalent to from 100 to 400 grams per liter of nickel sulfate heptahydrate, nickel chloride equivalent to from 10 to 75 grams per liter of nickel chloride hexahydrate, and from 10 to 50 grams per liter, preferably 15 to 40 grams per liter, of boric acid or other buffer such as formic acid or citric acid. To this fundamental solution there may be added in accordance with the present invention one or more aromatic sulfonamides to a concentration from ½ gram per liter to saturation, one or more coumarin compounds to a concentration from 0.01 to 0.5 gram per liter, and one or more leveling agents of the above indicated class in concentrations less than half a gram per liter, for example, from 0.0005 to 0.3 gram per liter. The concentrations of these compounds required for best results will be within the ranges indicated in the respective tables opposite each of said compounds, and very desirably will be approximately the specific concentration set forth opposite each compound in the tables.

The compounds listed in Table I are examples of sulfur compounds which when used in connection with coumarin and certain coumarin derivatives produce an increase in brightness with some loss in smoothness. Numerous other similar compounds produce the same effect in varying degree. They are aromatic sulfonamides and sulfimides. The compounds of Table II are examples of coumarin compounds which can be used. Alkyl and acyl derivatives of coumarin having 1 to 4 carbon atoms, and the chlorine and carboxy derivatives thereof are suitable. The compounds listed in Table III are examples of organic compounds effective to increase smoothing power (and brightness) of coumarin

type smoothing agents lost by the addition of sulfur compounds of the type of those listed in Table I. Coumarin sulfonic acids are not equivalent to the above indicated coumarin compounds.

Preferably, the solutions are operated in pH range from 2.5 to 4.5, the temperature is maintained within the range from 110° F. to 160° F., and the cathode current density is maintained within the range from 5 to 100 a. s. f.

Formaldehyde may be used in the above described solutions at a concentration of from 0.05 to 0.5 gram per liter for the purpose of retarding or minimizing the effect of breakdown products of coumarin or derivatives such as listed in Table II.

Specific examples which have yielded excellent results are indicated in Table IV.

Other basic solutions capable of yielding nickel ions for electrodeposition may be employed. Preferably there should be present in the solution at least one nickel salt of the class consisting of nickel sulfate, nickel chloride, nickel fluoborate and nickel sulfamate. The nickel ion concentration should in any case be within the range which would result from the presence of from 100 to 400 grams per liter of $NiSO_4.7H_2O$.

Table I

	Optimum Range, g./l.	Preferred Concentration, g./l.
(1) Benzene sulfonamide ($PhSO_2NH_2$)	0.5 to 3.0	1.0
(2) p-Toluene sulfonamide ($CH_3C_2H_4SO_2NH_2$)	0.5 to 3.0	1.0
(3) Saccharin (o-benzosulfimid)	0.5 to 3.0	1.0
(4) Dibenzene sulfonamide ($PhSO_2NHSO_2Ph$) and its mono-and-dichloro derivatives	0.5 to 5.0	1.0
(5) p-Benzene-bis (N-sylphonylbenzenesulfonamide) ($PhSO_2NHSO_2C_6H_4SO_2NHSO_2Ph$)	0.5 to 6.0	1.0
(6) N-ethane sulfonyl benzene sulfonamide	0.5 to 5.0	1.0
(7) Mono- and di-chlorobenzene sulfonamides	0.5 to 5.0	1.0
(8) Mono- and di-chloro derivatives of (2) and (5) above	0.5 to 5.0	1.0
(9) Bi-dibenzenesulfonamide ($PhSO_2NHSO_2C_6H_4C_6H_4SO_2NHSO_2Ph$)	0.5 to 5.0	1.0
(10) Mono- and di-chloro derivatives of (9) above	0.5 to 5.0	1.0
(11) Dibenzene sulfonamide ether ($PhSO_2NHSO_2C_6H_4OC_6H_4SO_2NHSO_2Ph$)	0.5 to 5.0	1.0

Table II

	Range, g./l.	Preferred Concentration g./l.
Coumarin	0.05 to 0.25	0.1
3-Chloro coumarin	0.05 to 0.25	0.1
6-Chloro coumarin	0.05 to 0.25	0.1
4-methyl coumarin	0.05 to 0.25	0.1
6-carboxy coumarin	0.05 to 0.25	0.1

Table III

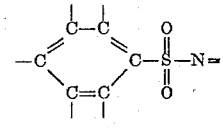
	Range, g./l.	Preferred Concentration, g./l.
(1) N,N'-(oxydiethylene)-bis-isoquinolinium chloride	0.003 to 0.01	0.005
(2) N,N'-(oxydiethylene)-bis-pyridinium chloride	0.003 to 0.01	0.007
(3) N-carboxymethyl pyridinium chloride	0.25 to 0.6	0.4
(4) N,N'-(oxydimethylene)-bis-pyridinium chloride	0.05 to 0.1	0.08
(5) Quinaldine methyl sulfate	0.05 to 0.1	0.08
(6) p-Xylylene pyridinium chloride	0.0025 to 0.015	0.005
(7) N-(2-chloroallyl) pyridinium chloride	0.05 to 0.12	0.08
(8) N-methallyl pyridinium chloride	0.05 to 0.12	0.08
(9) N,N' - methylene bis - pyridinium chloride	0.05 to 0.15	0.08
(10) N-(carboxy isobutyl) pyridinium chloride	0.03 to 0.1	0.05

Table IV

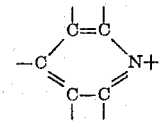
	Grams per Liter			
$NiSO_4.7H_2O$	300	300	300	300
$NiCl_2.6H_2O$	45	75	45	45
H_3BO_3	40	40	40	40
Sodium lauryl sulfate	0.2	0.06		
Coumarin	0.1	0.1	0.1	0.1
Saccharin		1.0		
Toluene sulfonamide				
Dibenzene sulfonamide			1.0	
Bi-dibenzene sulfonamide	1.0			1.0
N,N'-(oxydiethylene)-bis-pyridinium bromide	0.005	0.005		
N-carboxymethyl pyridinium chloride			0.25	

Having thus described the invention, what is claimed is:

1. A solution for electrodeposition of nickel in the form of bright and smooth deposits, said solution containing a nickel ion yielding compound of the class consisting of nickel sulfate, nickel chloride, nickel sulfamate and nickel fluoborate together with cooperating addition agents, one of said addition agents being an organic sulfur compound containing the group

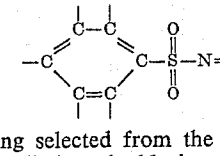


one thereof being selected from the class consisting of coumarin and its alkyl, acyl, chlorine and carboxy derivatives and a third thereof being a quaternary nitrogen compound containing the grouping

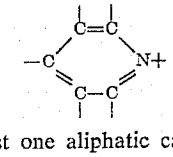


and having at least one aliphatic carbon atom attached to the nitrogen atom of said group, said first mentioned addition agent being present in concentration from one-half gram per liter to saturation, said second mentioned addition agent being present in concentration from 0.01 to 0.5 gram per liter and said third mentioned addition agent being present in concentration from 0.0005 to 0.3 gram per liter.

2. A process for producing bright, smooth electrodeposits of nickel comprising electrolyzing between an anode and a cathode a solution containing nickel sulfate equivalent to from 100 to 400 grams per liter of nickel sulfate heptahydrate, nickel chloride equivalent to from 10 to 75 grams per liter of nickel chloride hexahydrate and a group of three cooperating addition agents, one of said addition agents being an organic sulfur compound containing the group



one thereof being selected from the class consisting of coumarin and its alkyl, acyl, chlorine and carboxy derivatives and a third thereof being a quaternary nitrogen compound containing the grouping



and having at least one aliphatic carbon atom attached to the nitrogen atom of said group, said first mentioned addition agent being present in concentration from one-half gram per liter to saturation, said second mentioned addition agent being present in concentration from 0.01

to 0.5 gram per liter and said third mentioned addition agent being present in concentration from 0.0005 to 0.3 gram per liter.

3. A process according to claim 2 wherein said solution contains from 10 to 50 grams per liter of boric acid.

4. The invention as defined in claim 2 wherein said quaternary nitrogen compound is a bis-pyridinium compound.

5. The invention defined in claim 2 wherein said organic sulfur compound is bidibenzene sulfonamide.

6. The invention as defined in claim 2 wherein said quaternary nitrogen compound is an N,N'-(oxydiethylene)-bis pyridinium compound.

7. The invention as defined in claim 2 wherein said quaternary nitrogen compound is an N,N'-(oxydiethylene)-bis isoquinolinium compound.

8. The invention as defined in claim 2 wherein said quaternary nitrogen compound is an N,N'-(oxydiethylene)-bis pyridinium compound and said organic sulfur compound is bidibenzene sulfonamide.

9. The invention as defined in claim 2 wherein said quaternary nitrogen compound is an N,N'-(oxydiethylene)-bis isoquinolinium compound and said organic sulfur compound is bidibenzene sulfonamide.

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