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ELECTRODEPOSITION OF NICKEL

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This invention relates to electrodeposition of bright nickel by the use of a single brightening addition agent of the bis-pyridinium type or a mixture of equivalent addition agents of the same type.

Prior to the present invention it has been proposed to use compounds of the above class as brighteners in connection with auxiliary brighteners for acid nickel plating from a Watts type of solution. The maximum concentration, however, was thought to be about five one-hundredths of a gram per liter (five thousandths being considered better) inasmuch as greater amounts were found to embrittle the deposit, and the auxiliary brightener was thought essential.

I have now discovered that by using comparatively large concentrations of such addition agents as the sole brightener in an acid nickel plating solution I am able to produce deposits which are indeed brittle, but the brittleness of which is of a surprising and for many purposes unobjectionable type. When I first examined these deposits, which because they build brightness so rapidly may be called "quick bright" nickel, I thought them to be ductile without the usual aromatic sulfonate or sulfonamid. They do not produce the characteristic "cry" of the usual type of brittle deposits upon sharp bending, nor is there evidence of cracking visible to the naked eye. These deposits, as indicated, have the property of building brightness at a remarkably fast rate, so that relatively thin deposits on unbuffed or matte surfaces exhibit extreme brilliance, and they are characterized by excellent smoothing and scratch filling. On the other hand, microscopic examination indicates that these deposits are full of fine hair-line cracks not discernible by the naked eye. Adherence to steel is not good, but a 0.0001" to 0.0002" copper deposit on steel prior to "quick bright" nickel provides satisfactory adherence. Adherence to brass, copper and gray nickel electrodeposits is satisfactory.

Poor adherence and visible cracking of the deposit, which can be produced by too high concentrations of addition agent, are related not only to such concentration but also to the thickness of the deposit. For thin flash coatings for quick brightness building a high concentration of addition agent may be used. For thicker deposits to avoid stress cracking, lower concentrations are superior. Tests indicate that the appearance of the deposit is not altered after prolonged use of the solution. Carbon treatment of the solution after long use produces the ordinary gray nickel solution. The deposit exhibits microscopic cracks

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at the start and, as far as has been determined, retains this property indefinitely.

In salt spray corrosion comparisons with a commercial bright nickel deposit it was found that in the case of thin deposits (0.0001" to 0.0002") directly on steel the commercial deposit was much superior to the "quick bright" deposits of the same thickness. On copper deposits (0.4 to 0.8 mil) on steel there was no appreciable difference except that less green discoloration developed with the commercial nickel. In all the above cases the "quick bright" nickel is much brighter and smoother than the commercial "bright nickel" deposit. All of the corrosion panels were given an impact test with a drop weight, and in most cases it was found that nickel deposits according to the invention were superior to the commercial "bright nickel" in and around the impact depression.

Considering the difficulty of plating brass and particularly copper directly with chromium, it would appear commercially desirable to use the novel deposits as a flash coating on copper or brass prior to chrome plating. A flash coating over bright copper plated die castings gives an excellent appearing finish. Heavier thicknesses may be of practical value, but the extreme brightness obtainable in thin coatings would appear to be of more commercial interest. Thin coatings of the novel bright nickel over gray or semi-bright nickel have the advantage of improving the lustre although without improving the resistance to corrosion.

It is obvious that bright nickel according to the invention can be used effectively under circumstances where extreme brightness is desired, especially where it is desired to build brightness quickly, that is, using the least possible quantity of nickel. As is well known, the so-called bright copper is not normally as bright as commercial "bright nickel." It does, however, make a very excellent surface on which to deposit nickel plate according to the present invention. The nickel deposit builds up to full brightness when little more than a flash has been applied. The use of chromium over "quick bright" nickel over copper (preferably bright copper) over steel or zinc base die castings provides a laminated coating having good corrosion resistance, good adherence and a brilliant nickel color (due to brightening and smoothing action), while being economical of nickel and requiring no buffing. Bright nickel deposits according to the present invention may also be applied over gray nickel such as obtained from the Watts bath, or over semi-bright nickel

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such as obtained from a Watts bath modified by the addition of coumarin. Still other applications of the invention may be found feasible and advantageous.

The preferred basic solutions in connection with which the invention is realized are as follows:

TABLE I

All sulfate

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ -----	100 to 400, preferably 200 to 300 grams
Boric acid-----	0 to 60, preferably 10 to 40 grams
H_2O to make 1000 cc.	

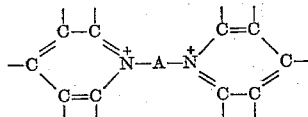
High chloride

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----	75 to 225, preferably 100 to 200 grams
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	50 to 150, preferably 75 to 150 grams
Boric acid-----	0 to 60, preferably 10 to 40 grams
H_2O to make 1000 cc.	

Sulfate-chloride (Watts type)

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ -----	100 to 400, preferably 200 to 300 grams
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	10 to 60, preferably 25 to 40 grams
Boric acid-----	0 to 50, preferably 15 to 40 grams
H_2O to make 1000 cc.	

To each of the foregoing basic solutions I add one or a mixture of compounds of the formula:



where A is a saturated or unsaturated chain made up of from 1 to 10 carbon atoms and from 0 to 2 oxygen atoms and the free valences are satisfied by hydrogen and from 0 to 4 hydrocarbon groups (one or two of which may serve to convert the pyridinium group to an isoquinolinium group, as shown by several examples in Table II below) containing in the aggregate for both pyridinium groups from 1 to 10 carbon atoms, the extra valences of the carbon atoms of A being satisfied by hydrogen and from 0 to 1 hydrocarbon groups containing in the aggregate from 1 to 6 carbon atoms, and where each hydrocarbon substituent group is attached to from 1 to 2 atoms of the group carrying such substituent group.

The following compounds are specific examples of the groups of addition agents above referred to, the same being utilized according to the invention in acid nickel plating solutions, preferably nickel sulfate and "mixed nickel sulfate and nickel chloride" solutions, suitably the basic solutions above set forth.

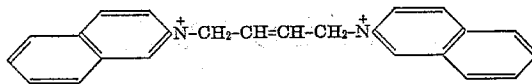
TABLE II

N,N' -ethylene-bis-pyridinium bromide
N,N' -trimethylene-bis-pyridinium bromide
N,N' -tetramethylene-bis-pyridinium bromide
N,N' -pentamethylene-bis-pyridinium bromide
N,N' -decamethylene-bis-pyridinium bromide
N,N' -methylene-bis-pyridinium bromide
N,N' -oxydimethylene-bis-pyridinium chloride
N,N' -oxyethylenemethylene-bis-pyridinium chloride
N,N' -oxydiethylene-bis-pyridinium chloride
N,N' -oxyditrimethylene-bis-pyridinium chloride
N,N' -methylene-bis-isoquinolinium chloride
N,N' -oxydimethylene-bis-isoquinolinium chloride
N,N' -oxyethylenemethylene-bis-isoquinolinium chloride
N,N' -oxydiethylene-bis-isoquinolinium chloride
N,N' -oxymethylene pyridinium chloride, ethylene isoquinolinium chloride
N,N' -oxydiethylene pyridinium isoquinolinium chloride
Propanone-1,3-bis-pyridinium chloride
N,N' -oxydipropylene-bis-pyridinium perchlorate

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N,N' -(oxydibutyl)-bis-pyridinium chloride
 N,N' -(oxydibutyl)-bis-isoquinolinium chloride
 N,N' -(2-butenylene)-bis-pyridinium bromide
 N,N' -(2-butenylene)-bis-isoquinolinium bromide

The last compound has the following structure:



The bromides and chlorides are fully equivalent to each other. No anti-pit agent is used, since no substantial pitting occurs.

These compounds are maintained in the acid nickel plating solution, preferably those above described, in concentration from 0.1 to 1.0 gram per liter, preferably from 0.2 to 0.75 gram per liter.

The following specific example will serve to illustrate the invention:

EXAMPLE I

A solution was made up containing:

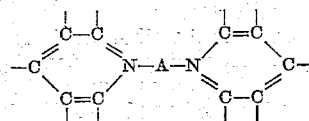
	Grams
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----	240
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	40
H_3BO_3 -----	40
N,N' -ethylene-bis-pyridinium bromide-----	0.4
H_2O to make one liter.	

This solution was operated at a pH of 3.5, a temperature of 140° F. and a cathode current density of 40 amperes per square foot. On a matte copper surface produced by electrodeposition copper on steel, extreme brilliance was achieved at a thickness of 0.000065 of an inch. On "bright" copper produced by electrodeposition from a commercial "bright copper" solution, extreme brilliance was achieved at a thickness of 0.00003 of an inch. On a vapor blasted steel panel having a roughness of RMS 34.5, "quick bright" nickel was deposited to a thickness of 0.0007 of an inch. The deposit exhibited an RMS of 6.6 and was fully bright.

On the bright copper above referred to, increasing the concentration of the addition agent to 0.75 gram per liter resulted in securing extreme brilliance at a thickness of 0.000015 of an inch, while decreasing it to 0.1 gram per liter resulted in securing extreme brilliance at 0.0005 of an inch.

Having thus described the invention, what is claimed is:

1. A nickel plating solution comprising an aqueous, acid solution of nickel material supplying nickel ions and an addition agent dissolved in said solution and capable of imparting to electrodeposits produced therein improved rates of increasing brightness with respect to increasing thickness of deposit, said solution consisting essentially of a composition from the class consisting of aqueous solutions of nickel sulfate and aqueous solutions of nickel sulfate and nickel chloride and said addition agent being at least one bis-pyridinium compound of the formula,



where A is a chain made up of from 1 to 10 carbon atoms and from 0 to 2 oxygen atoms and the free valences are satisfied by hydrogen and from 0 to 4 hydrocarbon groups containing in the aggregate for both pyridinium groups from 1 to 10 carbon atoms, the extra valences of the carbon atoms of A being satisfied by hydrogen and from 0 to 1 hydrocarbon groups containing in the aggregate

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from 1 to 6 carbon atoms, and where each hydrocarbon substituent group is attached to from 1 to 2 atoms of the group carrying such substituent group, said addition agent being present in solution to the extent of from 0.1 to 1.0 gram per liter.

2. The invention as defined in claim 1 wherein the concentration of said addition agent is from 0.2 to 0.75 gram per liter.

3. The invention as defined in claim 1 wherein the addition agent is N,N'-ethylene-bis-pyridinium bromide.

4. The invention as defined in claim 1 wherein the addition agent is N,N'-trimethylene-bis-pyridinium bromide.

5. The invention as defined in claim 1 wherein the addition agent is N,N'-tetramethylene-bis-pyridinium bromide.

6. The invention as defined in claim 1 wherein the addition agent is N,N'-pentamethylene-bis-pyridinium bromide.

7. The invention as defined in claim 1 wherein the addition agent is N,N'-methylene-bis-pyridinium bromide.

8. A nickel plating solution comprising an aqueous, acid solution of nickel material supplying nickel ions and an addition agent dissolved in said solution and capable of imparting to electrodeposits produced therein high rates of increasing brightness with respect to increasing thickness of deposit, said solution consisting essentially of nickel sulfate equivalent to from 100 to 400 grams of nickel sulfate heptahydrate per liter, nickel chloride equivalent to from 10 to 60 grams of nickel chloride hexahydrate per liter, boric acid up to 50 grams per liter, and said addition agent being selected from the class consisting of N,N'-ethylene-bis-pyridinium bromide, N,N' - trimethylene - bis - pyridinium bromide, N,N' - tetramethylene-bis-pyridinium bromide, N,N'-pentamethylene-bis-pyridinium bromide, N,N' - decamethylene - bis-pyridinium bromide, N,N'-methylene-bis-pyridinium bromide, N,N'-

oxydimethylene-bis-pyridinium chloride, N,N'-oxyethylenemethylene-bis-pyridinium chloride, N,N' - oxydiethylene - bis - pyridinium chloride, N,N'-oxyditrimethylene-bis-pyridinium chloride, N,N' - methylene - bis - isoquinolinium chloride, N,N' - oxydimethylene-bis-isoquinolinium chloride, N,N'-oxyethylenemethylene-bis-isoquinolinium chloride, N,N'-oxydiethylene-bis-isoquinolinium chloride, N,N'-oxymethylene pyridinium chloride, ethylene isoquinolinium chloride, N,N'-oxydiethylene pyridinium isoquinolinium chloride, propanone - 1,3 - bis-pyridinium chloride, N,N'-oxydipropylene-bis-pyridinium perchlorate, N,N'-(oxydibutyl)-bis-pyridinium chloride, N,N'-(oxydibutyl)-bis-isoquinolinium chloride, N,N'-(2-butenylene-bis-pyridinium bromide, N,N'-(2-butenylene)-bis-isoquinolinium bromide, said addition agent being present to the extent of from 0.2 to 0.75 gram per liter.

9. The invention defined in claim 8 wherein said addition agent is N,N'-ethylene-bis-pyridinium bromide.

10. The invention defined in claim 8 wherein said addition agent is N,N'-trimethylene-bis-pyridinium bromide.

11. The invention defined in claim 8 wherein said addition agent is N,N'-tetramethylene-bis-pyridinium bromide.

12. The invention defined in claim 8 wherein said addition agent is N,N'-pentamethylene-bis-pyridinium bromide.

13. The invention defined in claim 8 wherein said addition agent is N,N'-methylene-bis-pyridinium bromide.

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References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,513,280	Brown	July 4, 1950
2,550,449	Brown	Apr. 24, 1951