United States Patent Office

3,576,725

Patented Apr. 27, 1971

3,576,725

HIGH SPEED BRIGHT NICKEL PLATING AND ELECTROLYTE THEREFOR

Frank Passal, Detroit, Mich., assignor to M & T Chemicals Inc., New York, N.Y.

No Drawing. Filed June 7, 1963, Ser. No. 286,170
Int. Cl. C23b 5/08, 5/46
U.S. Cl. 204—49 4 Claims

ABSTRACT OF THE DISCLOSURE

A method of high speed electroplating bright nickel deposits. The bath comprises phenylpropiolamide as brightner and leveler and may additionally contain sulfo-oxygen compounds such as saccharin. High current densities and high electrolyte flow rates are used simultaneously to achieve a high rate of nickel deposition.

This invention relates to a novel process for electroplating. More specifically, it relates to high speed bright nickel plating.

As is well known to those skilled in the art, bright nickel plate may be obtained by plating from various types of baths, typically Watts-nickel baths, or modified Watts-nickel baths, or high-chloride nickel plating baths. Operation in these prior art baths typically may include plating from the nickel-containing solution at current densities which may be 1–10 amperes per square decimeter (hereinafter abbreviated as a.s.d.). Commonly these baths may contain a wide variety of brightening additives—usually a combination of two or more additives which are necessary to obtain a bright, leveled deposit.

Under normal prior art nickel plating conditions, it may be possible to attain the desired plate having a thickness of 0.2–2 mils in a period of time which depends upon the current density and other conditions of operation. (One mil is 0.001 inch or 0.0254 mm.) Commonly production of a 1 mil plate requires for example at least 15 minutes and possibly as long as one hour with the normally used current densities of 8 and 2 a.s.d., respectively. Normally nickel plating operations are conducted with little or moderate agitation i.e. low relative velocity between the bath and the cathode. Typically this may be effected by use of a slowly moving cathode bar, by air agitation, or combinations of both. Such agitation is normally sufficient to replenish the nickel ion content in the cathode film, at the current densities normally used.

Although it may be possible to obtain satisfactory bright nickel plate by use of such prior art systems, it has been found that production rates are undesirably low because of the time required, typically 30 minutes to attain a one-mil plate. Furthermore, because of this slow rate of plate deposition, it is necessary to employ relatively large tanks which cover an inordinately large amount of expensive floor space.

Typical prior art attempts which have been made to produce bright, leveled nickel deposits at high speed under varying conditions have included the use at high current densities of additive systems otherwise successful at ordinary plating speeds using low current densities. These have been unsuccessful because the prior art brightening systems did not permit attainment of high-speed, bright, and adequately leveled deposits over a wide current density range. These previous attempts to attain such deposits have involved the use of various cooperating additives including primary brighteners, secondary brighteners, or auxiliary brightening materials.

A secondary brightener may be a material which when added to a nickel plating bath in relatively high concentrations, typically 1–30 g./l., produces a plate which is characterized by a refined grain structure and moderate luster, but which is not highly reflective. A primary brightener may be a material which, when present in amounts of the general order of magnitude of 5–200 mg./l. and used simultaneously with a secondary brightener will permit attainment of a highly reflective deposit over a wide and useful current density range. In some systems, a third material, a secondary auxiliary brightener, usually in concentrations of 0.1–4 g./l. may be added to further enhance the luster and, particularly, leveling of the deposits.

Despite the numerous prior art attempts to develop a high speed bright nickel plating system which would have widely recognized advantages, there is today no commercially acceptable technique by which this can be accomplished. Although it may be possible by some processes to get an adequate degree of luster, it has not proven possible to concomitantly attain a high degree of leveling.

It is an object of this invention to provide a novel high speed technique for obtaining a bright nickel plate characterized by its high brilliance and extraordinary leveling. It is a further object of this invention to provide a high speed nickel plating system which may permit attainment of a ductile plate. Other objects will be apparent to those skilled in the art from inspection of the following description.

In accordance with certain of its aspects, the method of this invention for high speed electroplating a bright nickel deposit comprises electroplating said nickel deposit from a nickel bath containing a brightening and leveling amount of phenylpropiolamide, maintaining the cathode current density during said plating at a level of at least 10 a.s.d., and maintaining a high relative velocity between said nickel bath and said cathode thereby obtaining a highly lustrous, leveled nickel plate over a wide cathode current density range.

The nickel baths which may be employed in practice of this invention may include Watts-type baths, modified Watts-type baths, high-chloride baths, chloride-free baths, sulfamate-containing baths, etc. A typical Watts bath may have the following composition (here as elsewhere g./l. means grams per liter):

Component	Amount, g./l.	Preferred, g./l.
Nickel sulfate	250–500	300–400
Nlckel chloride	30–75	60–75
Boric acid	20–60	40–50

A typical modified Watts bath may have the following composition:

Component	Amount, g./l.	Preferred, g./l.
Nickel sulfate	250–500	300–400
Nickel chloride	75–150	100–130
Boric acid	20–60	40–50

The nickel sulfate used in the baths may be the commercial grade having 6–7 moles of water of crystallization per mole of $NiSO_4$; the nickel chloride may be that commercially available as the hexahydrate, $NiCl_2 \cdot 6H_2O$.

A typical chloride-free bath may have the following composition:

Component	Amount, g./l.	Preferred, g./l.
Nickel sulfate	250–500	300–400
Boric acid	20–60	40–50

In the above systems, soluble nickel anodes may be employed with the Watts or modified Watts baths. With the

chloride-free systems, the anodes may be either soluble or insoluble. If nickel is used as the anode, it is preferably of electrolytic nickel containing a controlled amount of sulfur, typically the SD type of nickel manufactured by International Nickel Co. This type of anode permits operation with minimum amount of polarization and oxygen evolution in chloride-free baths. If insoluble anodes are desired, it may be preferred to use lead as the anode material; and this may usually require replenishment of nickel content of the bath and reestablishment of proper bath pH by addition of a basic nickel compound e.g. nickel carbonate, nickel hydroxide, etc.

In practice of this invention it is preferred to add brightening and leveling quantities of phenylpropiolamide. Typically this compound, when employed as the brightening and leveling agent, may be present in amounts of at least 0.2 g./l. It is preferred to maintain this compound present in amount below its solubility limit, which, at typical operating temperatures of 60° C.–80° C., may be about 0.9–1.0 g./l. Thus commonly phenylpropiolamide may be present in amount of about 0.2–1.0 g./l. in the noted illustrative baths.

It is a feature of this invention that it may be possible to attain high-speed nickel deposits characterized by their extraordinary leveling characteristics together with extremely high brilliance by use of baths containing phenylpropiolamide alone i.e. as the sole brightening and leveling additive. In this embodiment, the brightening and leveling amount of phenylpropiolamide may be at least about 0.8 g./l. up to saturation. Saturation typically may be 0.9–1.0 g./l. depending upon the temperature, which may be within the range 60° C.–80° C.

It is a further feature of this invention that the nickel plating bath may be self-regulating as to maintenance of the additive concentration level, i.e. the phenylpropiolamide, when present as the sole additive, may be present in amount in excess of its solubility in which case the solid phase may dissolve as the compound is consumed from solution as by cathode effects including reductive action.

Preferably the solid may not be maintained in the solution proper, but may be maintained in a cartridge or filter through which the plating solution may pass e.g. as it is pumped to and from the plating bath.

A typical bath or solution may have the following composition:

Component	Amount, g./l.	Preferred, g./l.
Nickel sulfate	250–500	375
Nickel chloride	75–150	110
Boric acid	20–60	45
Phenylpropiolamide	[1] 0.8	0.9

[1] Saturation.

Another typical bath or solution may have the following composition:

Component	Amount, g./l.	Preferred, g./l.
Nickel sulfate	250–500	350
Boric acid	20–60	45
Phenylpropiolamide	[1] 0.8	0.9

[1] Saturation.

Another typical bath or solution may have the following composition:

Component	Amount, g./l.	Preferred, g./l.
Nickel sulfamate	240–400	325
Boric acid	20–60	45
Nickel chloride (optional)	7.5–45	15
Phenylpropiolamide	[1] 0.8	0.9

[1] Saturation.

It is a particular feature of certain aspects of this invention that it may be possible to attain a high-speed bright nickel deposit characterized by extraordinary degree of leveling, extremely high brilliance, and, particularly, by unexpectedly high ductility (especially in chloride-free systems) by use of baths containing phenylpropiolamide together with a secondary brightener. In this embodiment, the brightening and leveling amount of phenylpropiolamide may be 0.2–0.6 g./l., and typically 0.3 to 0.5 g./l. The preferred concentration of phenylpropiolamide may be 0.4 g./l.

Among the types of secondary brighteners which may be employed may be aromatic sulfonates, sulfonamides, sulfimides, or combinations thereof. Typical of the aromatic sulfonates may be benzene monosulfonate, naphthalene 1,3,6-trisulfonate, and naphthalene 1,5-disulfonate. Typical of the aromatic sulfonamides may be para-toluene sulfonamide and dibenzene sulfonamide. Typical of the aromatic sulfimides may be saccharin. When phenylpropiolamide is used in this embodiment together with a secondary brightener, the preferred secondary brighteners may include 1–4 g./l. of saccharin (Na salt) and 1–4 g./l. of dibenzene sulfonamide.

Typically the secondary brighteners may be present in concentration of 1–10 g./l., preferably 1–4 g./l. When the preferred secondary brightener, saccharin, is employed, it may be present in amount of 1–4 g./l.

A typical bath which may be used in practice of this embodiment of the invention may have the following composition:

Component	Amount, g./l.	Preferred, g./l.
Nickel sulfate	250–500	375
Nickel chloride	75–150	110
Boric acid	20–60	45
Phenylpropiolamide	0.2–0.6	0.4
Saccharin (Na salt)	1–4	3

Another typical bath which may be used in practice of this embodiment of the invention may have the following composition:

Component	Amount, g./l.	Preferred, g./l.
Nickel sulfate	250–500	350
Boric acid	20–60	45
Phenylpropiolamide	0.2–0.6	0.4
Saccharin (Na salt)	1–4	3

Another typical bath which may be used in practice of this embodiment of the invention may have the following composition:

Component	Amount, g./l.	Preferred, g./l.
Nickel sulfamate	240–400	325
Boric acid	20–60	45
Nickel chloride (optional)	7.5–45	15
Phenylpropiolamide	0.2–0.6	0.4
Saccharin (Na salt)	1–4	3

Another typical bath which may be used in practice of this embodiment of the invention may have the following composition:

Component	Amount, g./l.	Preferred, g./l.
Nickel sulfamate	240–400	325
Boric acid	20–60	45
Phenylpropiolamide	0.2–0.6	0.4
Saccharin (Na salt)	2–4	3

Another typical bath may have the following composition:

Component	Amount, g./l.	Preferred, g./l.
Nickel sulfate	250–500	375
Nickel chloride	75–150	110
Boric acid	20–60	45
Phenylpropiolamide	0.2–0.6	0.4
Dibenzenesulfonamide	1–4	4

In practice of this invention, a metal cathode which has been precleaned and which may have been copper plated may be placed within a nickel plating bath together with either a soluble anode or an insoluble anode as hereinbefore described. Typical preferred temperature of the bath during plating may be 60° C.–80° C.

In the preferred practice of this invention, the baths are preferably maintained at a pH of 2–5, preferably 3.5–4.5, say 4. It is a concomitant advantage of the additive systems of this invention that the baths are operative over a very wide pH range in contrast to prior art brightener systems where much more limited pH ranges are necessary. This insensitivity to pH is of particular importance where insoluble anodes are used, necessitating pH adjustment with a basic nickel compound. Since these basic nickel compounds are most highly reactive below pH 3.5 it is highly advantageous to be able to operate substantially below pH 3.5. It is not necessary to use wetting or anti-pitting agents when plating according to this invention thereby minimizing problems which might arise therefrom because of e.g. foaming, decomposition products of wetting agents, etc.

During plating, the cathode current density will preferably be maintained at a level of at least about 10 a.s.d. Preferably it will be found that the high-speed bright nickel plating process of this invention may be effected at a current density of 20–120, preferably 20–60 a.s.d. Plating carried out in accordance with this novel technique may permit deposition of predetermined thicknesses of bright, leveled nickel in a time which is as little as 10% or less of the time required when using standard processes presently available. Typically production of a bright nickel plate 1 mil thick by the process of this invention may require 3 minutes in contrast to 30 minutes for prior art plating processes. The rate of plating may typically be 1–3 minutes per mil of bright nickel plate.

The novel technique of this invention includes the step of maintaining a high relative velocity between the nickel bath and the cathode. It may be possible to maintain this high relative velocity which serves to replenish the cathode film with nickel ions as they are plated out therefrom, by use of a bath which contains agitation means sufficient to maintain a substantially homogeneous catholyte. Typically this may be accomplished by use of high speed mixers in the solution.

It is preferred to maintain the high relative velocity between the nickel bath and the cathode at a level equivalent to about 60–320, say 150 cm./second. These velocities may be produced e.g. by varied techniques such as vibration (including ultrasonic) or rotation of the cathode relative to the solution, by pumping the electrolyte e.g. catholyte through the system and over the cathode surface, by very vigorous agitation of the electrolyte by appropriately positioned propellers or other devices, etc.

In the preferred embodiment, the high relative velocity may be maintained by impinging the nickel bath against the cathode. This may be effected by impinging a stream of electrolyte uniformly against those portions of the cathode which are to be plated. In the preferred embodiment, this may be effected by directing a stream of electrolyte, as from a conduit, onto the noted portions of the cathode. If desired, a plurality of streams may be directed onto the cathode surface. Preferably in one embodiment the stream of electrolyte from the conduit may be directed against the cathode in manner to sweep the cathode surface and thereby provide fresh catholyte over the area to be plated. Preferably the impinging stream may contact the cathode at a high rate.

The nickel plate obtained by the process of this invention may be characterized by its high brightness. Typically the deposit is highly reflective over a wide current density range, and free of striations and/or hazy areas, and/or other imperfections. The luster obtained is at least comparable in every way to that obtained under normal low speed plating conditions even with the best available bright nickel additive systems.

The plate obtained by the process of this invention may be further characterized by its high leveling. Typically a one mil deposit, plated at e.g. 40–60 a.s.d., will substantially obliterate scratches produced by one single pass of zero-grit emery paper when plating is effected under high speed conditions during a period of two minutes. With the best bright nickel systems of the prior art, the best plate attainable will merely give either only partial or no obliteration of the scratch lines when the plate is deposited for the same period of time.

When phenylpropiolamide is used in combination with a secondary brightener, typically saccharin, the plate may possess an unexpectedly high ductility. This high ductility is particularly attainable when the plate is deposited from chloride-free systems. The high ductility can be produced over a reasonably wide range of concentration of phenylpropiolamide. Prior art brightener combinations permit attainment of ductile plate only under relatively narrow and difficultly controllable concentration limits of primary brighteners.

It is a feature of this invention that the additives used may be readily determined and controlled by spectrophometric analyses in the ultraviolet region. The additives may be particularly characterized by high degree of stability under conditions of operation; any decomposition products formed do not undesirably affect the plating characteristics of the system.

Practice of this invention according to certain of its aspects may be observed from the following examples wherein all parts are expressed in grams per liter (g./l) unless otherwise indicated.

In the examples, bright high-speed nickel may be plated from a bath having the following composition:

Component	Amount, g./l.
Nickel sulfate	300
Nickel chloride	120
Boric acid	45
Additive-brightener	As noted infra.
Temperature	65° C.
pH	As noted.

In each example, the solution was passed through a conduit obliquely onto one end of the surface of a vertically positioned brass electrode with the section to be plated 13.5 cm. long and 1.9 cm. wide, to give an exposed cathode area of 25.7 cm.^{2}. On the front of this highly polished brass cathode there was inscribed a longitudinal 1 cm. wide single pass of zero-grit emery scratches centrally positioned on the cathode surface. The back of the cathode was sealed by means of a plastic backing. The velocity of the impinging stream was about 150 cm./second. The angle of the downwardly flowing stream was 45° to the vertical.

The outer periphery of the cathode was bounded by plastic barriers or shields extending outwardly from the cathode thereby effecting channelling of the electrolyte as it passed over the cathode. This entire assembly was submerged in a body of electrolyte. Cathode contact was made to that section of the strip, not to be plated, which extended out of the solution. A slab of SD nickel was positioned parallel to the cathode at a distance of 20 cm. The times of plating used were 3 minutes (except for Example 4 where the time was 2 minutes) to give a deposit thickness of one mil. In the examples, the additive was varied.

In the following examples, the pH in Examples 1–9 was 4 except for Example 5 where the pH was 5. The current density in these examples was 40 a.s.d. except for Example 4 where it was 60 a.s.d.

Example Number	Additive	Amount, g./l.	Comments
1	Phenylpropiolamide	0.6	Slight haze; highly leveled.
2	do	0.8	Uniformly brilliant; all scratch marks virtually obliterated.
3	do	[1] 0.9	Do.
4	do	[1] 0.9	Do.
5	do	[1] 0.9	Do.
6	Phenylpropiolamide	0.3	Uniformly brilliant; all scratch marks virtually obliterated good ductility.
	Saccharin	1.6	
7	do	0.4	Do.
	do	1.6	
8	do	0.6	Do.
	do	3.2	
9	Phenylpropiolamide	0.4	Do.
	Dibenzene sulfonamide	3.0	

[1] Saturation.

In the following examples, the bath had the following composition:

Component:	Amount, g./l.
Nickel sulfate	375.
Boric acid	45.
Additive	As noted.
Temperature	65° C.
pH	As noted.
Current density	40 a.s.d.

Example Number	Additive	Amount, g./l.	pH	Comments
10	Phenylpropiolamide	0.3	4	Brilliant, highly leveled, ductile deposit.
	Saccharin	1.6		
11	do	0.4	4	Do.
	do	2.5		
12	do	0.6	4	Do.
	do	2.5		
13	do	0.6	3.5	Do.
	do	2.5		
14	Phenylpropiolamide	0.4	4.5	Do.
	Dibenzene sulfonamide	3.0		
15	Phenylpropiolamide	0.4	3	Do.
	Saccharin	2.0		
16	do	0.4	2	Do.
	do	2.0		

In the following examples, the bath had the following composition:

Component:	Amount, g./l.
Nickel sulfamate	350.
Boric acid	45.
Additive	As noted.
Temperature	65° C.
pH	As noted.
Current density	40 a.s.d.

Example Number	Additive	Amount, g./l.	pH	Comments
17	Phenylpropiolamide	0.9	3.5	Brilliant, highly leveled, ductile deposit.
18	do	0.4	3	Do.
	Saccharin	1.6		

When examining the deposits using phenylpropiolamide as the sole additive (Examples 1–5) the deposits appeared to have tensile stress. Those deposits obtained with combinations of phenylpropiolamide and a secondary brightener appeared to have lower tensile stress. However, in the chloride-free bath (Examples 10–18) the stress was found to be either low tensile or slightly compressive, depending on the phenylpropiolamide concentration, which is highly desirable when the plated part is to be subjected to mechanical and thermal stresses during use. In the chloride-free baths of the examples, the ductility was also markedly improved as mentioned previously.

It will be apparent that the novel nickel baths of this invention, which may contain as additive a composition selected from the group consisting of (a) at least 0.8 g./l. of phenylpropiolamide and (b) a secondary brightener together with 0.2–0.6 g./l. of phenylpropiolamide, permit attainment of a high speed bright nickel plate.

It will be apparent that this invention has been described with respect to specific examples and various modifications will be apparent to those skilled in the art.

I claim:

1. The method of high speed electroplating a bright nickel deposit which comprises electroplating said nickel deposit from a nickel bath containing soluble nickel salts and a primary brightener consisting essentially of a brightening and leveling quantity of phenylpropiolamide as the sole brightening and leveling additive present in brightening and leveling amount of at least 0.8 g./l., maintaining the cathode current density during said plating at a level of at least 10 a.s.d. and maintaining a high relative velocity between said nickel bath and said cathode, thereby obtaining a highly lustrous leveled nickel plate over a wide cathode current density range.

2. The method of high-speed electroplating a bright nickel deposit as claimed in claim 1 wherein phenylpropiolamide is present in brightening and leveling amount of 0.8 g./l. to saturation.

3. The method of high-speed electroplating a bright nickel deposit characterized by extraordinary leveling and high brilliance which comprises electroplating said nickel deposit from a nickel bath containing soluble nickel salts and a primary brightener consisting essentially of at least 0.8 g./l. of phenylpropiolamide, maintaining the cathode current density at 20–60 a.s.d. during said plating, and maintaining a high relative velocity between said nickel bath and said cathode.

4. An aqueous electroyltic nickel bath for high-speed electrodeposition of bright nickel plate consisting essen-

tially of 250–500 g./l. nickel sulfate, 20–60 g./l. boric acid, and at least 0.8 g./l. of phenylpropiolamide.

References Cited

UNITED STATES PATENTS

2,781,305	2/1957	Brown	204—49
2,879,211	3/1959	Kardos et al.	204—49
2,994,648	8/1961	Du Rose	204—49
3,139,393	6/1964	Hartman et al.	204—49

2,363,973	11/1944	Kennedy et al.	204—25
2,870,709	1/1959	Boelter, Jr.	204—3

OTHER REFERENCES

Wesley, W. A. et al.: "Electrodeposition of Nickel at High Current Density," 36th Annual Proceedings of the American Electroplaters Society, pp. 79–91, 1949, TS 670 A32.

GERALD L. KAPLAN, Primary Examiner