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PROCESS OF ELECTRODEPOSITING HARD NICKEL PLATING

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The present invention relates to a process of electrodepositing hard nickel plating, and, more particularly, to a process of rapidly electrodepositing nickel plating of extremely high hardness.

Heretofore attempts have been made to provide the art with a process of producing hard nickel plating. Thus, Fescol, Ltd. of England employed abroad a process by which moderately hard nickel plating might be accomplished. Among the disadvantages of this process the most serious are the extreme slowness and the limitation on the hardnesses of the plate produced. Other suggestions have been made by prior investigators including D. J. Macnaughtan and coworkers whose researches are set forth in the Transactions of the Faraday Society for the years 1931 and 1933. The Macnaughtan experiments contemplated the production of nickel plating of higher hardnesses. This process likewise had the disadvantage of extreme slowness and required long periods of time to produce thick nickel deposits. Other attempts and proposals have been made to solve the outstanding problem, but, so far as I am aware, none has been made which was capable of being carried into practice on an industrial scale for the production of commercial articles having thick nickel plate of high hardness and at a rapid rate.

I have discovered a process which solves the problem confronting the art and which is capable of producing hard nickel plate at rapid rates.

It is an object of the invention to provide an improved method for the electrodeposition of hard nickel having a hardness of at least 400 Vickers and at controlled temperatures and current densities having a critical correlation to the hydrogen ion concentration of the plating bath whereby such hard nickel plates can be produced at relatively rapid rates.

It is a further object of the invention to provide a process of nickel electroplating to repair worn machinery and to produce new parts for resistance to wear and to combined corrosion and wear.

The invention also contemplates the provision of a method for the electrodeposition of nickel plate having high hardnesses in excess of about 400 Vickers and at a critically controlled temperature of at least 100° F. and a current density of at least about 25 amperes per square foot and at a hydrogen ion concentration pH of about 5.4 to about 6.1. The present process makes possible the deposition of a layer of hard nickel having a thickness as great as about 0.125 inch at a rapid rate.

It is also within the contemplation of the invention to provide a method for the electrodeposition of sound hard nickel plate free from cracks, fissures and other defects from an aqueous plating bath containing as essential ingredients a nickel salt and an ammonium salt under controlled and correlated critical plating conditions.

Other objects and advantages of the invention will become apparent from the following description.

Generally speaking, the present invention provides a process for the production of hard nickel plating by electrodeposition from an aqueous plating bath containing as essential ingredients an ionizable nickel salt, e. g., nickel sulphate and/or nickel chloride to provide nickel cations, and an ammonium salt such as ammonium sulphate and/or chloride. Other ingredients may also be present for buffering the solution, increasing conductivity, etc., as those skilled in the art will readily appreciate. The desired hard nickel plating, e. g., having a hardness in excess of about 400 Vickers, may be deposited from such a solution under certain critical plating conditions involving correlation and control of pH, bath temperature and current density within critical limits or ranges. The pH should be within the range of about 5.4 to 6.1 and preferably about 5.5 to 5.9, and in some cases about 5.8 to 5.9. Unless otherwise indicated, pH values are based on determinations made with the quinhydrone electrode. A bath temperature of at least about 100° F. is necessary, and the bath may be operated satisfactorily at much higher temperatures, e. g., up to about 150° F. If the temperature is raised substantially above this level it is generally too high for satisfactory commercial application. Ordinarily an operating temperature within the range of about 110° F. to about 140° F. is preferred. To obtain satisfactory hard deposits at commercially practicable rates under the foregoing conditions, the cathode current density should not be appreciably less than about 25 amperes per square foot and I prefer to operate at a current density of at least about 50 amperes per square foot up to about 150 amperes per square foot. By operating the plating bath within the aforementioned limits of pH, bath temperature and current density, satisfactory electrodeposited nickel plating having a hardness of at least about 400 Vickers can be produced at a rapid rate under commercial conditions and on an industrial scale.

The following aqueous plating baths have been

used in electrodepositing nickel having a hardness in excess of 400 Vickers.

Bath Composition A

	Grams per liter, about
Nickel sulphate	120
Ammonium sulphate	20
Potassium chloride	8

Bath Composition B

	Grams per liter, about
Nickel sulphate	120
Ammonium sulphate	20
Potassium chloride	8
Ammonium chloride	6

Bath Composition C

	Grams per liter, about
Nickel sulphate	90
Nickel chloride	30
Ammonium sulphate	16
Ammonium chloride	4.5
Potassium chloride	6
Boric acid	30

Bath Composition D

	Grams per liter, about
Nickel sulphate	180
Ammonium chloride	25
Boric acid	30

Bath Composition E

	Grams per liter, about
Nickel chloride	102
Ammonium chloride	17
Potassium chloride	8

(Those skilled in the art can readily calculate in a known manner that the nickel concentration of baths suitable for the present process, as illustrated by the foregoing bath compositions, is within the range of about 25 grams per liter to about 38 grams per liter, that the ammonia [(NH_4)] content is within the range of about 5 grams per liter to about 8.5 grams per liter, and that the chlorine concentration is within the range of about 3.8 grams per liter to about 46 grams per liter.) It is to be understood that these bath compositions are merely illustrative examples and that the relative amounts of the ingredients may vary over considerable ranges. In using bath A, for example, it was found that varying the nickel sulphate concentration from 120 to 150 grams per liter, other conditions being the same, caused no appreciable change in the hardness of the deposit. Similarly the particular nickel or ammonium salt or salts used to supply the nickel and ammonium cations may vary depending upon economic factors, type of base metal to be plated, and other considerations well understood by those skilled in the art. The choice of the buffering agent to be employed for facilitating pH control as well as the selection of agents to increase bath conductivity and/or to improve dissolution of the nickel anode, if any, are governed by the ordinary factors that must be weighed in determining the bath composition for general plating work.

In order to give those skilled in the art a better understanding of the invention and of the benefits and advantages that may be obtained by practicing the same, illustrative data are summarized in the following table:

Table I

Bath composition	Temp.	Current[1] density	pH	Deposit thickness	Time	Hardness, Vickers
	°F.			Inch	Hours	
A	117–124	50	5.7–5.8	.025	10	420–440
A	130	75	5.8	.03	7	440
A	155	150	5.8	.05	6	440
D	110	50	5.4	.013	5	430
D	110	50	5.75	.008	3	507
D	120	50	5.4	.025	10	402
D	120	50	5.8	.01	4	485
D	120	50	5.9	.01	4	508
D	130	50	5.5	.026	10	400
D	130	50	5.8	.013	5	463
D	140	50	5.6	.008	3	400
D	140	50	5.9	.008	3	458
E	110	50	5.8	.015	6	409
E	110	50	5.95	.03	12	440
E	120	50	6.0	.014	5.5	430

[1] Amperes per square foot.

The base on which the deposits referred to in Table I were made was steel having a Vickers hardness of about 260. If a copper base is used with bath A the hardness of the deposit may be lower. For example, the following results were obtained on a copper base having a hardness of about 60 Vickers:

Table II

Specimen	Deposit thickness	Deposit hardness, Vickers
	Inch	
No. 1	0.006	227
No. 2	0.012	250

Instead of plating at one operation to a thickness of 0.012 inch, a third specimen similar to No. 1 was plated with an additional layer about 0.006 inch thick, and the hardness of this deposit was 430 Vickers. This gives a simple solution to the problem of getting high deposit hardness on relatively soft base or foundation metals. The hardness of the deposit from bath D is not affected to so great an extent by the hardness of the base as deposits from bath A. Thus the hardness of deposits on comparable steel and copper bases from bath D under a given set of plating conditions were 400 and 370, respectively, as compared with 468 and 227, respectively, for a different set of plating conditions with bath A.

Pitting of the deposit may tend to occur under certain conditions unless suitable precautions, well known to those skilled in the art, are taken, e. g., the addition of small amounts of hydrogen peroxide. I have also discovered that increasing the chloride content of the bath decreases the tendency toward pitting. In an all chloride bath, such as bath E, pitting is negligible, even without taking special precautions to prevent or minimize it. When the plating is to be performed on a steel base, the base metal must be relatively free of surface defects. This condition can be achieved by resurfacing the base metal by machining or with emery, or it can be attained by coating the base with a thin layer of electrodeposited copper.

I have discovered that a critical correlation exists between temperature and current density and that it is necessary to utilize the new combination of temperature and current density in

conjunction with a special control of the hydrogen ion concentration (pH) in order to produce sound nickel deposits having Vickers hardness of about 400 or higher. The following table sets forth illustrative examples of the relation of pH, temperature and current density that have produced the hardnesses specified:

Table III

Bath	Temperature	Current density	pH	Hardness, Vickers
	°F.	*Amperes/square ft.*		
A	120	50	5.6	400
A	120	50	5.8	440
A	130	75	5.8	440
A	155	150	5.8	440
D	110	50	5.4	430
D	120	50	5.6	450
D	140	50	5.8	440
E	130	50	6.0	400

With the foregoing conditions, the hard nickel plate is electrodeposited at extremely rapid rates as indicated by the following table:

Table IV

Current density	Time required to deposit a layer 0.1 inch thick
Amperes/square ft.	*Hours*
50	38
75	25
100	19
150	13

In distinct contrast to the new results obtained by my process, the prior art employed a current density of about 10 amperes per square foot and required 192 hours (8 days) to deposit a layer about 0.1 inch thick.

Baths A and B require rather close attention in order to maintain the proper pH value. Under some circumstances deposits from baths A and B, particularly heavy deposits, may show distinct laminations, traceable probably to fluctuation in pH adjacent to the face of the plating, i. e., at the cathode film. Baths B, C, D and E corrode the anode somewhat better than bath A. Baths C, D and E have better buffer characteristics than baths A and B and consequently require less constant attention to pH. Laminated deposits have not been observed in deposits from baths C, D and E. The stress is higher in deposits from bath E than in deposits from the other baths under comparable operating conditions. Under ordinary conditions, bath D is preferable because of its simplicity, good buffer characteristics, ease of pH control, relatively low deposit stress, uniform depth of deposit, comparatively slight tendency to form large weak trees at the edges and corners of the cathode, and other favorable characteristics. In operating bath D, if it is found necessary to raise the pH, ammonia should not be used as the solubility of nickel ammonium sulphate may be exceeded and the salt crystallize out. Although bath D is preferred for general use, it should be pointed out that all bath compositions listed above are capable of producing adherent, hard nickel deposits at a rapid rate when operated under the plating conditions disclosed hereinabove. Numerous experiments with the foregoing illustrative and other bath compositions indicate that satisfactory hard deposits are obtained with an aqueous bath containing salts yielding nickel and ammonium cations.

The present invention provides a means for producing nickel coatings of extreme hardness, a hardness greater than has been commercially achieved, so far as I know, with conventional processes for electrodepositing nickel or any alloy rich in nickel. The coatings made by the present new method are sound and can be made in great thicknesses at speeds fast enough to be commercially economical as indicated by the foregoing tables. The toughness of hard nickel and the adherence of it to steel are superior to those of conventional chromium deposits. Large paper mill rolls which have been plated with chromium for resistance to wear and corrosion have been unsatisfactory because chromium deposits were too brittle, did not adhere well to cast iron and steel bases, and tended to spall with use. A heavy hard nickel coating made in accordance with the present process and finished, if desired, with a thinner layer of chromium, provides a superior roll. Other useful applications may be made of the present process. Thus, the present process makes it practicable to reclaim worn machine elements by building up the worn parts with the new hard, wear-resistant nickel deposits. As a specific instance of machine elements that may be reclaimed in this manner may be mentioned Diesel engine crankshafts such as are used in the modern streamlined trains. The chemical art is interested in the present process for coating cams which must operate immersed in corrosive solutions and for coating large solid nickel hopper jaws used in the production of plastic sheets. These jaws have knife edges which must withstand combined corrosion and wear.

In some cases where it is desired to increase the ductility of the deposit, the plated object may be heat treated in substantially the same manner as cold worked nickel except that a somewhat lower temperature should be used. Hard nickel deposits have a lower softening temperature than wrought nickel. A temperature of about 500° F. has been found satisfactory to relieve internal stress appreciably and thus increase the ductility without substantially lowering the hardness and tensile strength.

It is to be noted that earlier attempts to produce thick deposits of high hardness encountered frequent cracking of the plated layer due to ignorance of the principles of the present invention and the critical relationships between the controllable variables of temperature, current density and the hydrogen ion concentration involved in the present discovery. Variation in the bath composition, in accordance with the foregoing disclosure, may also be made to assure the proper structure and mechanical properties of the hard plating for the particular application.

Furthermore, the prior art failed to produce nickel deposits of even moderately high hardnesses at cathode current densities above about 15 amperes per square foot. In contrast to the prior art my new process produces nickel coatings of high hardness at current densities above 100 amperes per square foot.

Moreover, the prior art disclosed no method for producing sound deposits of hardnesses consistently and practically, especially for commercial products on an industrial basis, above about 360 Vickers (350 Brinell), whereas the present process accomplishes this and in addition yields deposits of controllable high hardness.

The present application is a continuation in part of my copending application Serial No. 131,866, filed March 19, 1937.

Although the present invention has been described in some detail in conjunction with certain specific illustrative examples and preferred embodiments, it will be understood by those skilled in the art that modifications of bath composition and variotions in procedure may be made without departing from the spirit and scope of the invention as defined in the subjoined claims.

I claim:

1. A process for rapidly electro-depositing nickel plating of extremely high hardness and of good adherence on a base having a hardness of at least about 227 Vickers which comprises establishing a nickel electroplating bath comprising an aqueous solution containing at least 25 grams per liter of nickel provided by at least one electrolyte-soluble nickel electroplating salt yielding nickel cations and at least 5 grams per liter of ammonia provided by at least one ammonium salt yielding ammonium cations, adjusting the pH of said nickel electroplating bath within a range of about pH 5.4 to about pH 6.1 (quinhydrone) to provide suitable acidity in said bath without crystallizing and the like, maintaining the temperature of said bath within a range of at least 100° F. to about 155° F. and electro-depositing nickel at a cathode current density within a range of about 25 emperes per square foot to about 150 amperes per square foot at a cathode having a hardness of at least about 227 Vickers disposed in said bath whereby an extremely hard nickel plate is consistently produced having a satisfactory hardness of at least about 400 Vickers at a commercially practicable rapid rate of at least about 0.1 inch in about thirty-eight hours.

2. A process for rapidly electro-depositing nickel plating of extremely high hardness and of good adherence on a base having a hardness of at least about 60 Vickers which comprises establishing a nickel electroplating bath comprising an aqueous solution containing at least 25 grams per liter of nickel provided by at least one electrolyte-soluble nickel electroplating salt yielding nickel cations and at least 5 grams per liter of ammonia provided by at least one ammonium salt yielding ammonium cations, adjusting the pH of said nickel electroplating bath within a range of about pH 5.4 to about pH 6.1 (quinhydrone) to provide suitable acidity in said bath without crystallizing and the like, maintaining the temperature of said bath within a range of at least about 100° F. to about 155° F. and electro-depositing nickel at a cathode current density within a range of about 25 amperes per square foot to about 150 amperes per square foot at a cathode having a hardness of about 60 Vickers disposed in said bath until a nickel electroplating having a hardness of about 227 Vickers is obtained on said cathode and then electro-depositing a second layer of nickel from said bath at a current density within the aforesaid range and at a temperature within the aforesaid temperature range until a second nickel electroplate having a hardness of at least 400 Vickers is obtained whereby an extremely hard nickel plate having a satisfactory hardness of at least about 400 Vickers is consistently produced on a base having a hardness of about 60 Vickers at a commercially practicable rapid rate of at least about 0.1 inch in about thirty-eight hours.

3. A process for rapidly electro-depositing nickel plating of extremely high hardness and of good adherence on a base having a hardness of at least about 227 Vickers which comprises establishing an aqueous nickel electroplating bath containing at least 25 grams per liter of nickel provided by at least one electrolyte-soluble nickel electroplating salt yielding nickel cations and at least 5 grams per liter of ammonia provided by at least one ammonium salt yielding ammonium cations, adjusting the pH of said nickel electroplating bath within a range of about pH 5.5 to about pH 5.9 (quinhydrone) to provide suitable acidity in said bath without crystallizing and the like, maintaining the temperature of said bath within a range of at least 110° F. to about 140° F. and electro-depositing nickel at a cathode current density within a range of about 50 amperes per square foot to about 150 amperes per square foot at a cathode having a hardness of about 227 Vickers disposed in said bath whereby an extremely hard nickel plate is consistently produced having a satisfactory hardness of at least about 400 Vickers at a commercially practicable rapid rate of at least about 0.1 inch in about thirty-eight hours.

4. A process for rapidly electro-depositing nickel plating of extremely high hardness and of good adherence on a base having a hardness of at least about 227 Vickers which comprises establishing a nickel electroplating bath comprising an aqueous solution containing about 180 grams per liter of nickel sulfate, about 25 grams per liter of ammonium chloride and about 30 grams per liter of boric acid, adjusting the pH of said nickel electroplating bath within a range of about pH 5.5 to about pH 5.9 (quinhydrone) to provide suitable acidity without crystallizing and the like, maintaining the temperature of said bath within a range of about 110° F. to about 140° F., and electro-depositing nickel at a cathode current density within a range of about 25 amperes per square foot to about 100 amperes per square foot at a cathode having a hardness of about 227 Vickers disposed in said bath whereby an extremely hard nickel plate is consistently produced having a satisfactory hardness of at least about 400 Vickers at a commercially practicable rapid rate of at least about 0.1 inch in about thirty-eight hours.

5. A process for rapidly electro-depositing nickel plating of extremely high hardness and of good adherence on a base having a hardness of at least about 227 Vickers which comprises establishing a nickel electroplating bath containing at least 25 grams per liter of nickel provided by at least one electrolyte soluble nickel electroplating salt yielding nickel cations and at least 5 grams per liter of ammonia provided by at least one ammonium salt yielding ammonium cations, said bath having a pH of about pH 5.4 to about pH 6.1 (quinhydrone) and being substantially devoid of crystals and the like within the aforesaid pH range and electro-depositing nickel at a cathode current density within a range of about 25 amperes per square foot to about 150 amperes per square foot at a cathode having a hardness of about 227 Vickers disposed in said bath while maintaining the temperature of said bath within a range of at least 100° F. to about 155° F. whereby an extremely hard nickel plating is consistently produced hav-

ing a satisfactory hardness of at least about 400 Vickers at a commercially practicable rapid rate of at least about 0.1 inch in about thirty-eight hours.

6. A process for rapidly electro-depositing nickel plating of extremely high hardness and of good adherence on a base having a hardness of at least about 227 Vickers which comprises establishing a nickel electroplating bath comprising an aqueous solution containing at least one electrolyte-soluble nickel electroplating salt capable of yielding nickel cations selected from the group consisting of nickel sulfate, nickel chloride and mixtures thereof and at least one electrolyte-soluble ammonium salt capable of yielding ammonium ions selected from the group consisting of ammonium sulfate, ammonium chloride and mixtures thereof, said bath containing about 25 grams per liter to about 38 grams per liter of nickel, about 5 grams per liter to about 8.5 grams per liter of NH_4 and about 3.8 grams per liter to about 46 grams per liter of chlorine, having a pH of about pH 5.4 to about pH 6.1 (quinhydrone) and being substantially devoid of crystals and the like within the aforesaid pH range, and electro-depositing nickel at a cathode current density within the range of about 25 amperes per square foot to about 150 amperes per square foot at a cathode having a hardness of about 227 Vickers disposed in said bath while maintaining the temperature of said bath within the range of at least 100° F. to about 140° F. whereby an extremely hard nickel plate is consistently produced having a satisfactory hardness of at least about 400 Vickers at a commercially practicable rapid rate of at least about 0.1 inch in about thirty-eight hours.

7. A process as set forth and described in claim 6 in which at least a portion of the chlorine present in said bath is provided by a chloride selected from the group consisting of chlorides of sodium and potassium.

8. In the process for producing electrodeposits of hard nickel comprising electro-depositing nickel in an aqueous nickel electroplating bath having a pH of about pH 5.4 to about pH 6.1 (quinhydrone) and being substantially devoid of crystals and the like within the aforesaid pH range and containing at least 25 grams per liter of nickel as an electrolyte-soluble nickel electroplating salt capable of yielding nickel cations and at least 5 grams per liter of ammonia in the form of an ammonium salt capable of yielding ammonium cations, the improvement which comprises employing a cathode current density of about 25 amperes per square foot to about 150 amperes per square foot and a temperature of at least 100° F. to about 155° F. whereby an extremely hard nickel plate having a satisfactory hardness of at least about 400 Vickers and of good adherence is consistently produced on a base having a hardness of at least about 227 Vickers at a commercially practicable rapid rate of at least about 0.1 inch in about thirty-eight hours.

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