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ELECTROPLATING DUPLEX NICKEL COATINGS

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This invention relates to electroplating, and is particularly directed to the provision of an improved nickel electroplating process for producing a nickel electroplate of duplex structure having enhanced capability of protecting underlying metal from corrosion.

In recent years there has been increased utilization of bright nickel electroplating processes, which result in the formation of smooth bright to brilliant nickel electroplates that require little or no buffing to attain a high degree of surface luster. Such deposits are of great advantage in producing decorative nickel-plated or chromium-plated articles, because they greatly reduce or eliminate altogether the laborious polishing and buffing operations which formerly were required to produce brilliant finishes.

Bright nickel electroplates are produced by incorporating a brightening addition agent in the electroplating bath. By the term "brightening addition agent" we mean a strong brightening agent which promotes the formation of an electrodeposit having a brighter and more lustrous surface than the basis metal itself prior to electrodeposition agents which merely inhibit degradation of the surface brightness as a result of the electrodeposition are not considered brightening addition agents for purposes of this invention. A wide variety of brightening addition agents have been developed in recent years. A small but significant concentration of such agents must be maintained in the plating bath at all times in order to produce bright nickel electroplates, and it is characteristic of them that they are consumed, by codeposition or reduction, during electrolysis. While these addition agents are highly useful for imparting brightness and a leveling effect to the electrodeposit, they have a notable tendency, when used in concentrations adequate to produce the generally desired high degree of brightness, to reduce ductility of the electroplate and to increase its internal stress. So-called "carrier" brighteners, such as water-soluble sulfonic acids and other sulfo-oxygen compounds, which are not brightening addition agents of the character defined above and which exert no leveling effect on the electrodeposit, have been found useful in combination with strong brightening agents to minimize brittleness and internal stress in a bright electrodeposit, and to extend the current density range over which bright deposits may be formed. However, their use has the disadvantage of tending to decrease the effectiveness of the deposit for protecting the underlying metal against corrosion.

The optimum characteristics of bright nickel deposits with respect to internal stress, ductility and corrosion resistance have not been fully realized in a single coating. Duplex coatings, consisting of first, a semi-bright deposit, followed by a fully bright layer, have been proposed heretofore, and by forming them it has been possible to produce an electrodeposit of satisfactory brilliancy and with physical properties and corrosion resistance better than are obtained in a single bright deposit alone of the same thickness. However, up to the present time it has been necessary to deposit the two different layers in separate plating solutions under different conditions and bath compositions.

Our present invention provides a plating method whereby duplex coatings of high brilliancy, low stress, good ductility, and good corrosion resistance are produced in one and the same plating solution contained in a single tank. This result is achieved by taking advantage of the fact that the effect of brightening addition agents, especially when they are used in small amounts, on the appearance, crystal structure, and physical and chemical properties of the nickel electrodeposits depends upon the degree of agitation of the solution; i.e., the effects of these addition agents are diffusion controlled. In carrying out our method, the article to be electroplated is introduced into the electroplating bath, and the deposition of nickel thereon is begun. The bath is maintained substantially quiescent in the vicinity of the article until a substantial nickel electroplate has been formed. Thereafter, and without withdrawing the article from the bath or discontinuing the deposition of nickel thereon, the bath in the vicinity of the article is subjected to vigorous agitation until a further substantial deposit of nickel has been electroplated on the article.

This method of the invention is particularly adapted for use in commercial electroplating operations which are carried out in apparatus utilizing a conveyor system for carrying articles to be plated through the plating operation, and usually also through the sequence of cleaning and rinsing operations which precede and follow the actual plating operation. In such an operation, in accordance with our invention, the article to be plated is introduced into the plating bath and is advanced while immersed therein through a path of travel to a point in the bath remote from the point of introduction of the article; and nickel is continuously electrodeposited on the article as it advances through such path of travel. The bath adjacent the point of introduction of the article, and throughout an initial portion of its path of travel, is maintained substantially quiescent; whereas the bath is vigorously agitated throughout the region of a later portion of the path of travel of the article.

It has been observed that when an electroplate of nickel is deposited on a base metal by the method of our invention, the initial portion of the deposit which is formed where the bath is maintained substantially quiescent possesses a generally columnar or fibrous microstructure. On the other hand, the section of the deposit formed in that portion of the bath which is vigorously agitated displays a lamellar microstructure. Electrodeposits having this duplex structure have been found to provide particularly good protection against corrosion of the underlying metal when the plated article is subjected to a corrosive environment. And, of particular significance to commercial electroplating operations, this improved duplex electroplate is formed from a single plating bath, in a single electroplating operation, without introducing any significant process or apparatus complication into the plating system.

A presently preferred embodiment of the method of our invention is carried out as follows: A nickel electroplating bath is established in the plating tank of an automatic plating conveyor system. The bath may be any conventional nickel-plating bath, for example, a standard Watts bath containing nickel salts, boric acid, brightening agent, and whatever other addition agents are desired, dissolved in water. Nickel anodes are immersed in the electrolyte and are connected to the positive terminal of a plating generator or other direct current power source.

Articles to be plated are deposited on conveyor racks, and are carried by the conveyor into and through the body of electrolyte in the plating tank. The articles on

the rack, while they are being carried through the plating bath, are electrically connected to the negative terminal of the plating generator or other power source. The conveyor advantageously is so arranged that it lowers the article to be plated into the plating tank adjacent one end thereof, then slowly advances it while it remains immersed in the plating bath to a point adjacent the other end of the tank, and then lifts the article from the tank and carries it thence through rinsing, washing and other finishing operations.

The above-described plating procedure and plating apparatus are not in themselves novel features of our invention. But in accordance with our invention, provision is made for subjecting a portion only, and not the whole, of the body of electrolyte in the plating tank to vigorous agitation; i.e. the electrolyte is vigorously agitated adjacent the end of the tank from which the plated articles are withdrawn, but the portion of the electrolyte adjacent the end of the tank where such articles are introduced is maintained substantially unagitated. For example, the electrolyte throughout the final 50% to 25% of the path of travel of the article through the plating tank may be vigorously agitated; whereas the electrolyte throughout the first 50% to 75% of the path of travel of the article is maintained relatively quiescent.

Any conventional agitating means may be employed for imparting the desired agitation to the agitated portion of the plating bath. For example, mechanical agitators may be mounted in the plating tank in the region where the bath is to be agitated; or air injection pipes or nozzles may extend into the bath in the region where the bath is to be agitated, so that such portion of the bath may be subjected to vigorous air agitation; or solution circulation pumps may be arranged to provide vigorous local agitation by means of turbulent circulation of the electrolyte. No agitating means, however, extend into the plating tank in the region where the bath is not to be agitated. By operating such mechanical agitators or pumps, or by delivering a stream of air through such nozzles, vigorous agitation is imparted to the electrolyte in contact with the article while the final portion of the nickel electrodeposit is formed thereon; at the same time that portion of the bath through which the article passes during formation of the initial portion of the electrodeposit is maintained substantially quiescent. It is of course true that there is no sharp boundary between the agitated and quiescent portions of the bath; and the relatively quiescent portion is not devoid of convection currents or other motion. So far as the effect of the agitation on the plating operation is concerned, however, the bath in the latter portion of the plating cycle functions as one which is vigorously agitated, while it functions as a quiescent bath in the region where the initial portion of the plating cycle is carried out.

It is generally necessary in the operation of bright nickel plating baths to add make-up brightening agents continuously or at periodic intervals to maintain an adequate concentration of such agent in the bath. In carrying out the present invention, the duplex character of the electro-deposit which is formed on the article being plated can be made more pronounced, and a brighter surface is produced on the finished article, if the make-up brightening agent is added to the agitated portion of the bath. For example, such additions may with advantage be made near the place where the plated articles are withdrawn from the plating bath. The vigorous agitation of the bath at and near the withdrawal end of the tank insures rapid and effective dissemination of the make-up brightening agent throughout the agitated portion of the bath. Convection currents that unavoidably occur in the unagitated portion of the bath suffice to insure that an adequate concentration of make-up brightening agent is carried into and disseminated throughout the unagitated portion of the bath.

Often it is the practice to incorporate a wetting agent in nickel electroplating baths, in order to insure intimate contact of the electrolyte with the article being plated over its entire surface and to minimize the formation of tiny pits in the electroplate. Such agents, like the brightening agents, tend to be consumed during the course of the electrolysis. When such agents are used in electroplating baths operated in accordance with this invention, it is preferable to add make-up amounts thereof to the unagitated portion of the bath, preferably near where the articles to be plated are introduced. Thereby maximum concentration of this agent is maintained where it is needed most, while the convection currents referred to suffice to distribute and maintain adequate concentrations thereof throughout the unagitated region of the bath, and to deliver a portion of such agents into the agitated portion of the bath.

In the preferred embodiment of the invention described above, a duplex electrodeposit is formed on the article in consequence of maintaining one portion of the bath substantially quiescent while vigorously agitating the remainder of the bath. It is of course evident that triplex and other multiplex deposits may be formed by maintaining three or more successive portions of the bath under differing conditions of quiescence or agitation, or even under differing degrees of agitation. Also, it is evident that the duplex or multiplex character of the deposit may be made more pronounced by maintaining in the different portions of the bath differences in such other variable conditions of operation as temperature and cathode current density.

Particularly desirable results have been achieved when using the method of this invention in the production of bright nickel-plated articles from a plating bath containing, as a brightening agent, 2-butyne-1,4-diol, or other water-soluble acetylenic compound, particularly though not necessarily when used in combination with a water-soluble sulfonic acid or other sulfo-oxygen compound, as described in the Kardos, Menzel and Sweet U.S. Patent No. 2,712,522. Following is an example of this invention as carried out using a plating bath containing a brightening agent of this character: An aqueous Watts nickel-plating bath of the following composition was prepared:

	Grams per liter
Nickel sulfate, $NiSO_4.6H_2O$	300
Nickel chloride, $NiCl_2.6H_2O$	45
Boric acid, H_3BO_3	40
2-butyne-1,4-diol	0.12
Sodium naphthalene trisulfonate	7.5
Wetting agent	0.04

The bath was heated to a temperature of about 50° C., and had a pH of 3.0. A steel panel was immersed in the bath, and with the bath in quiescent condition, nickel was electroplated thereon for a period of ten minutes at a current density of 60 amperes per square foot. Then, without removing the panel from the electrolyte or otherwise discontinuing or interrupting the nickel-plating operation, the bath in the vicinity of the panel was subjected to vigorous air agitation. Plating in the agitated electrolyte continued at substantially the same current density for a further period of ten minutes. The panel was then withdrawn from the bath and inspected. It was found to have a fully bright and highly ductile nickel electrodeposit, of duplex structure comprising a lamellar formation superposed on a columnar formation, over its entire area. Thereafter, an electrodeposit of chrominum 0.00001 inch in thickness was applied to the panel by a conventional chromium-plating operation. The resulting chromium-plated panel was subjected to accelerated corrosion tests and the results compared with those obtained on corresponding chromium-plated panels which had been initially nickel plated under the conditions described above but with agitation of the bath throughout the entire twenty-minute period of nickel plating, and on which the

nickel deposit possessed a substantially uniform lamellar structure throughout its thickness. The corrosion resistance of the panel having the duplex structure was notably superior to the corrosion resistance of the control panel on which the nickel electroplate was of substantially uniform character throughout its thickness. Using the number of rust spots formed per unit of area on the two panels in the course of the accelerated corrosion test as an index of corrosion resistance, the former showed only one to two rust spots per square inch, whereas the latter, even when prepared under the most carefully regulated plating conditions and using only carefully filtered nickel electrolyte, showed at least ten to fifteen rust spots per square inch.

Although the improved results which are attained by the method of this invention have been particularly exemplified above with reference to a Watts type nickel-plating bath containing an acetylenic alcohol as the brightening agent, the invention is not limited in its utility to plating operations carried out using such bath, or such brightening agent. On the contrary, the benefits of the invention can be attained when employed in conjunction with any nickel electroplating bath, including, but without limitation, nickel chloride plating baths, nickel sulfate plating baths, nickel sulfamate plating baths, and nickel fluoborate baths. The presence in or absence from such baths of wetting agents, anti-foaming agents, and other agents for imparting particular characteristics to the bath, are immaterial so far as the present invention is concerned. And the advantages of the invention are realized (in some degree at least) with all brightening addition agents of the character hereinbefore defined, including in addition to acetylenic alcohols but without limitation, the following: unsaturated N-oxide compounds, e.g., pyridine-N-oxide; aromatic phosphinic acid compounds, e.g., phenyl phosphinic acid; alpha-amino-N-heterocyclic compounds, e.g., alpha-amino pyridines; bis-pyridyl compounds, e.g., 2,2'-dipyridyl; olefinic alcohols, e.g., butene-diol; and acetylenic amines, e.g., propargyl amines and 1-diethylamino-2-propyne.

Examples of brightening addition agents which have been used successfully in carrying out the method of this invention are listed in Table I. Each of the agents listed in the table was used in a Watts bath having the composition (with respect to nickel salts, boric acid and wetting agent) given above, in the concentration given in the table. In each case a duplex electroplate was formed by first electroplating an initial deposit of nickel on a basis metal at 50° C. and at 40 amperes per square foot of cathode area without agitating the bath in the vicinity of the cathode, and then electroplating a further deposit of

Table I

Brightening Addition Agent		Other Agent Present	
Name	Concentration, g./l.	Name	Concentration, g./l.
Pyridine-N-oxide	0.01	Saccharin	2
Benzenephosphinic acid.	0.05	Naphthalene-trisulfonic acid, sodium salt.	7.5
2-Amino-6-methyl-pyridine.	0.01-0.02	Saccharin	1-2
Dipyridyl amine	0.005-0.01	do	1-2
2,2'-Dipyridyl	0.001	do	2
2-Butene-1,4-diol	0.1		
Do	0.1	Naphthalene trisulfonic acid, sodium salt.	7.5
1,4-bis(diethylamino)-2-butyne.	0.1	Thiomalic acid	0.04
Do	0.1	Naphthalene trisulfonic acid, sodium salt.	7.5
Pyridylethyl sulfonic acid.	0.1	Saccharin	2

nickel at the same temperature and current density but with vigorous agitation of the bath in the vicinity of the cathode.

We claim:

1. The method of producing a nickel electroplate of duplex structure having enhanced capability of protecting underlying metal from corrosion which comprises establishing a substantially unagitated aqueous nickel electroplating bath in which a brightening addition agent is incorporated, introducing an article to be electroplated into the unagitated bath, said bath being substantially quiescent in the vicinity of said article, and electrodepositing nickel of a generally columnar, fibrous microstructure until a substantial nickel electroplate has formed on the article, and thereafter, without withdrawing said article from the bath and without discontinuing the deposition of nickel thereon, subjecting said bath in the vicinity of the article to vigorous agitation until a further substantial amount of nickel of a lamellar microstructure has been electroplated on said article.

2. The method according to claim 1, in which the brightening addition agent comprises 2-butyne-1,4-diol.

3. The method according to claim 1, in which the brightening addition agent comprises a water-soluble acetylenic alcohol and a water-soluble sulfo-oxygen compound.

4. The method of producing a nickel electroplate of duplex structure having enhanced capability of protecting underlying metal from corrosion which comprises establishing an aqueous nickel electroplating bath in which a brightening addition agent is incorporated, subjecting a portion only of said bath to vigorous agitation while maintaining another portion thereof unagitated and substantially quiescent, introducing an article to be electroplated into the unagitated and substantially quiescent portion of said bath and advancing it therethrough and into and through the agitated portion of the bath, and continuously electrodepositing nickel on said article while it is being advanced through both the unagitated and substantially quiescent and the agitated portions thereof, whereby nickel of a generally columnar, fibrous microstructure is electrodeposited in the unagitated and substantially quiescent portion of the bath and nickel of a lamellar microstructure is electrodeposited in the vigorously agitated portion of the bath.

5. The method according to claim 4, in which, as the brightening addition agent is consumed, make-up brightening addition agent is added to the agitated portion of the bath.

6. The method according to claim 4, in which the brightening addition agent comprises 2-butyne-1,4-diol.

7. The method according to claim 5, in which the brightening addition agent comprises 2-butyne-1,4-diol.

8. The method according to claim 4, in which the brightening addition agent comprises a water-soluble acetylenic alcohol and a water-soluble sulfo-oxygen compound.

9. The method according to claim 5, in which the brightening addition agent comprises a water-soluble acetylenic alcohol and a water-soluble sulfo-oxygen compound.

10. The method according to claim 4, in which a wetting agent is present in the bath to minimize pit formation in the electrodeposit formed on the article, and in which, as such wetting agent is consumed, make-up amounts thereof are added to the unagitated portion of the bath in the vicinity of the point of introduction of the article.

References Cited in the file of this patent

UNITED STATES PATENTS

2,312,517 Baker ..... Mar. 2, 1943
2,712,522 Kardos et al. ..... July 5, 1955

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,879,211 March 24, 1959

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, list of references cited, after line 73, insert the following:

FOREIGN PATENTS

526,966 Great Britain - - - - Sept. 30, 1940

Signed and sealed this 21st day of July 1959.

(SEAL)

Attest:
KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents