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ELECTROREFINING NICKEL

3,114,687

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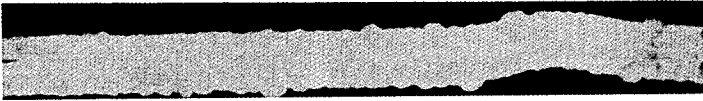


Fig. 1.

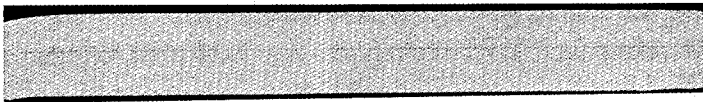


Fig. 2.

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ELECTROREFINING NICKEL

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4 Claims. (Cl. 204—112)

The present invention is directed to the electrorefining of nickel and, more particularly, to an improved method for producing electrolytic nickel or cathode nickel having improved surface quality.

The method for electrorefining nickel using impure nickel metal anodes is described in U.S. Patent No. 2,394,874 and the method for electrorefining nickel using nickel matte anodes is described in U.S. Patent No. 2,839,461. In the method described in each of these patents, the electrorefining cell employed is a compartmented cell divided into anode and cathode compartments by means of a permeable diaphragm and the electrolyte employed is a sulfate-chloride electrolyte. The impure anode in the anode compartment is electrolytically corroded and substantially pure cathode nickel is deposited at a cathode in the cathode compartment as a result of electrolysis. The impure anolyte is removed from the anode compartment at a steady rate and is subjected to purification treatments to remove therefrom impurities such as iron, copper, lead, arsenic, etc. The purified electrolyte is then introduced at a steady rate into the cathode compartment and nickel of high purity is plated therefrom. A slight hydrostatic head is maintained in the cathode compartment, allowing purified catholyte partly depleted in nickel to flow through the diaphragm into the anode compartment, thus preventing migration of unwanted ions from the impure anolyte in the anode compartment to the purified catholyte in the cathode compartment. As the process proceeds, nickel and impurities are dissolved from the anode. The impure anolyte is removed from the tanks, purified, and finally returned as purified catholyte to each cathode compartment for the deposition of pure nickel at each cathode.

It has been found that the cathode nickel produced in accordance with commercial practice tends to have a surface which becomes progressively more rough and nodular as the thickness of the cathode increases or as the current density is increased. This roughness and nodularity effectively limits the current density at which nickel cathodes can be grown and the thickness of cathode nickel which can be produced by means of the electrorefining process. Thus, it has been a long sought objective in nickel electrorefining to produce smoother and thicker electrolytic nickel at higher current densities because of the inherent economic advantages at the refinery and because such nickel would be more acceptable as an article of commerce. Although many attempts have been made to overcome the foregoing difficulties and to provide smoother, thicker electrolytic nickel, none was entirely successful when carried out on a commercial scale.

It has now been discovered that electrolytic nickel cathodes having an improved surface smoothness and greater thickness as compared to prior nickel cathodes can be produced in an electrorefining operation by the addition of controlled amounts of a special organic compound to the purified electrolyte.

It is an object of the present invention to provide a process for producing nickel cathodes having improved surface smoothness.

Another object of the invention is to provide a bath from which nickel cathodes having improved surface smoothness may be deposited by electrolysis.

Still another object of the invention is to provide a

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method for producing nickel cathodes which are thicker and smoother than nickel cathodes produced heretofore.

Yet another object of the invention is to provide a method for producing nickel cathodes which are thicker and smoother than conventional cathodes at current densities higher than those of conventional practice.

Other objects and advantages will become apparent from the following description taken in conjunction with the accompanying drawing, in which:

FIGURE 1 is a reproduction of a photograph taken at 1½ diameters showing the cross section of the usual electrolytic nickel cathode presently available in commerce; and

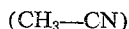
FIGURE 2 is a reproduction of a photograph taken at 1½ diameters of the cross section of an electrolytic nickel cathode produced in accordance with the present invention to a greater thickness than the cathode shown in FIGURE 1.

Generally speaking, the present invention contemplates a process for the production of electrolytic nickel or cathode nickel having improved surface quality and including improved surface smoothness which comprises electrolyzing an aqueous electrolyte having a pH of about 1 to 5 containing about 40 to about 60 or 70 grams per liter of nickel, about 12 to 30 grams per liter of sodium, from about 18 to 55 grams per liter of chloride ions, from 65 to 120 grams per liter of sulfate ions, from about 10 to 25 grams per liter of boric acid and about 0.01 to about 0.10 gram per liter of a water-soluble organic cyanide (nitrile), i.e., a compound containing the $\text{—C}\equiv\text{N}$ group, attached to a C atom, dissolved therein to deposit sound electrolytic nickel at the cathode. The electrolysis is carried out while maintaining the electrolyte temperature between about 100° F. and about 160° F. and while employing a current density between about 5 and about 25 amperes per square foot. The catholyte may contain a total of up to about 0.004 gram per liter of such impurities as copper, iron, arsenic, lead, etc., without affecting the operating characteristics of the process. In addition, the catholyte may be saturated with respect to calcium ions. Thus, it may contain up to about 0.6 gram per liter of calcium, without affecting the operating characteristics of said process. The process utilizing the aforementioned electrolyte is applicable not only to the production of commercial cathode nickel but also to the production of the thin nickel cathode starting sheets employed in producing commercial cathode nickel.

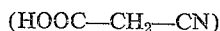
In carrying the invention into practice to produce cathode nickel having improved surface quality and including improved surface smoothness, it is advantageous to electrolyze an aqueous catholyte having a pH of about 4.0 to 5.0 and containing about 40 to about 70 grams per liter of nickel, about 20 to about 30 grams per liter of sodium, about 65 to about 120 grams per liter of sulfate ions, about 20 to about 55 grams per liter of chloride ions, about 10 to about 25 grams per liter of boric acid and about 0.01 to about 0.05 gram per liter of ethylene cyanohydrin (hydracrylonitrile) dissolved therein and the balance essentially water to deposit nickel at the cathode. The electrolysis is carried out by passing electric current through an anode (which, as explained before, may be either an impure nickel anode or a nickel matte anode), the electrolyte and the cathode (usually a nickel starting sheet) while maintaining the temperature between about 130° F. and about 140° F. and while employing a current density between about 10 to about 25 amperes per square foot. The process is also operable when utilizing insoluble anodes. The concentration of the special organic cyanide compound contemplated in accordance with the present invention is governed largely by current density but should be at least about 0.01 gram per liter

because at lower concentrations improvement in the surface quality of cathode nickel is negligible. It should not exceed about 0.10 gram per liter as otherwise the purity of cathode nickel is detrimentally affected by carbon co-deposition and the cathodes become highly stressed and/or warped. Stresses set up in the nickel deposited on the stainless steel mother blanks to form the cathode starting sheets and due to excessive amounts of the aforementioned compounds are often so great that the cathode nickel separates from the mother blanks and the resulting starting sheets are badly warped. Attempts to straighten the warped starting sheets are defeated by their "springy" reaction due to the high stresses. The production of the commercial cathode nickel is also adversely affected when excessive amounts of the additives are employed in that the cathodes become highly stressed and warped and difficulty is encountered in extricating these warped cathodes from the cathode compartments and in thereafter straightening them.

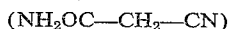
Other organic cyanide (nitrile) compounds within the scope of the present invention include acetonitrile



acrylonitrile ($\text{CH}_2=\text{CH}-\text{CN}$), acetaldehyde cyanohydrin ($\text{CH}_3-\text{CHOH}-\text{CN}$), cyanoacetic acid



acetone cyanohydrin ($(\text{CH}_3)_2-\text{COH}-\text{CN}$), propionitrile ($\text{CH}_3-\text{CH}_2-\text{CN}$), 2 cyanoacetamide



beta-chloropropionitrile ($\text{ClCH}_2-\text{CH}_2-\text{CN}$), benzonitrile ($\text{C}_6\text{H}_5-\text{CN}$) and para amino phenyl aceto nitrile ($\text{NH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{CN}$). From the foregoing, it will be seen that the organic cyanides suitable within the scope of the invention may be saturated or unsaturated, aliphatic or aromatic and may contain a substituted group such as a halogen, hydroxy, amino or carboxy group. Numerous additional examples could be given but the examples given above will suffice to illustrate the class of compounds suitable within the scope of the invention.

For the purpose of giving those skilled in the art a better understanding of the invention, the following illustrative examples are given:

Example I

To a portion of a purified electrolyte having a pH of about 4.0 and containing about 55 grams per liter of nickel, about 28 grams per liter of sodium, about 46 grams per liter of chloride ion, about 87 grams per liter of sulfate ions, about 18 grams per liter of boric acid, about 0.3 gram per liter of calcium ion and less than about 0.004 gram per liter total of copper, lead, arsenic and iron, about 0.035 gram per liter of ethylene cyanohydrin was added. The electrolyte was then electrolyzed to deposit cathode nickel at a current density of about 15 amperes per square foot and a temperature of about 140° F. Nickel from the said electrolyte was deposited upon both faces of a nickel starting sheet in order to grow a cathode having a total thickness of about 0.4 inch. The cathode was found to have a high degree of surface smoothness (such as illustrated in FIGURE 2) whereas a cathode grown from the same electrolyte without the addition of ethylene cyanohydrin was found to have a surface which was substantially more rough, nodular and "berried" (such as shown in FIGURE 1) when grown to the same thickness of about 0.4 inch.

Example II

To another portion of the same electrolyte, an addition of about 0.035 gram per liter of ethylene cyanohydrin as a surface-smoothness promoting agent was made. The electrolyte was then electrolyzed to deposit cathode nickel upon both faces of a thin nickel starting sheet used as a cathode. The cathode was grown to the substantially

greater thickness of about 0.8 inch. The surface of the resulting cathode was substantially smoother than the prior art cathode even though it had been grown to a thickness about twice as great as its customary for commercial electrolytic nickel.

The presence of organic cyanide compounds in the electrolyte in the amounts contemplated in accordance with the present invention does not interfere with the production of ductile high purity cathode nickel. Thus, cathode nickel produced in accordance with the invention from a purified sulfate-chloride nickel electrolyte is substantially indistinguishable chemically from cathode nickel produced heretofore. Furthermore, no difficulties are encountered in maintaining the required concentration of the organic cyanide compound in the plating bath and no difficulties are found in the purification cycle as a result of the addition to the bath of the organic cyanide compound. As is usual in the electrorefining of nickel, sulfur-containing organic compounds which are reducible at the cathode should not be present in the electrolyte provided in accordance with the present invention as sulfur would be incorporated in the nickel deposit, thus impairing the high standard of purity of the cathode nickel.

While the mechanism involved in the present invention is not fully understood theoretically since the invention relates to a complex electrolyte and process in which many phenomena, including electrolysis, ionization, ion migration, hydrolysis, etc., are or may be encountered, it has nevertheless been found that the addition of minute amounts of a water-soluble nitrile in accordance with the invention to the electrolyte used for electrorefining, electrowinning, etc., has the remarkable effect that the nickel deposited at the cathode is greatly improved in surface appearance and smoothness. It is to be understood that the water soluble nitrile compounds employed in accordance with this invention need only be soluble in the electrolyte to the extent determined by the amount required. However, it is an advantage from the operating standpoint to employ those nitrile compounds which are soluble in water to the extent of about 10 grams per liter or more.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Thus, it is to be understood that the invention is applicable in all types of nickel electrorefining electrolytes, including the all-chloride and the all-sulfate electrolytes as well as the sulfate-chloride electrolyte. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

I claim:

1. In the method for electrorefining impure nickel material, the improvement for producing electrolytic nickel having substantial thickness, high purity and improved surface smoothness which comprises establishing an aqueous catholyte having a pH of about 1 to 5 and consisting of about 40 to about 70 grams per liter of nickel, about 12 to about 30 grams per liter of sodium, about 18 to 55 grams per liter of chloride ions, about 65 to 120 grams per liter of sulfate ions, about 10 to 25 grams per liter of boric acid, about 0.01 to 0.10 gram per liter of a water-soluble organic cyanide compound selected from the group consisting of ethylene cyanohydrin, acetonitrile, acetaldehyde cyanohydrin, cyanoacetic acid, acrylonitrile, acetone cyanohydrin, propionitrile, 2 cyanoacetamide, beta-chloropropionitrile, para amino phenyl aceto nitrile and benzonitrile dissolved therein, the balance of said catholyte being essentially water and electrolyzing said catholyte while maintaining the temperature thereof between 100° and 160° F. by passing electric current at a current density between about 5 and about 25 amperes per square foot through said catholyte to a starting sheet made of metal

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from the group consisting of nickel and stainless steel immersed in said catholyte to deposit sound electrolytic nickel of high purity and having a smoother surface than electrolytic nickel produced from the same bath having no addition of said organic cyanide.

2. The method according to claim 1 wherein the organic cyanide is ethylene cyanohydrin.

3. In the method for electrorefining impure nickel material, the improvement for producing electrolytic nickel having substantial thickness, high purity and improved surface smoothness which comprises establishing an aqueous catholyte having a pH of about 4 to 5 and consisting of about 40 to 70 grams per liter of nickel, about 20 to 30 grams per liter of sodium, about 65 to 120 grams per liter of sulfate ions, about 20 to 55 grams per liter of chloride ions, about 10 to 25 grams per liter of boric acid, about 0.01 to 0.05 gram per liter of a water-soluble organic cyanide compound selected from the group consisting of ethylene cyanohydrin, acetonitrile, acetaldehyde cyanohydrin, cyanoacetic acid, acrylonitrile, acetone cyanohydrin, propionitrile, 2 cyanoacetamide, beta-chloropropionitrile, para amino phenyl aceto nitrile and benzonitrile dissolved therein, the balance of said catholyte

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being essentially water and electrolyzing said catholyte while maintaining the temperature thereof between about 130° and 140° F. by passing electric current at a current density of about 10 to 25 amperes per square foot to a starting sheet made of metal from the group consisting of nickel and stainless steel immersed in said catholyte to deposit sound electrolytic nickel of high purity and having a smoother surface than electrolytic nickel produced from the same bath devoid of said organic cyanide.

4. The method according to claim 3 wherein the organic cyanide is ethylene cyanohydrin.

References Cited in the file of this patent

UNITED STATES PATENTS

15	2,394,874	Renzoni	Feb. 12, 1946
	2,524,010	Du Rose	Sept. 26, 1950
	2,623,848	Renzoni	Dec. 30, 1952
	2,802,779	Cowle et al.	Aug. 13, 1957
	2,882,208	Becking et al.	Apr. 14, 1959
20	2,972,571	Towie	Feb. 21, 1961
	2,978,391	Du Rose	Apr. 4, 1961