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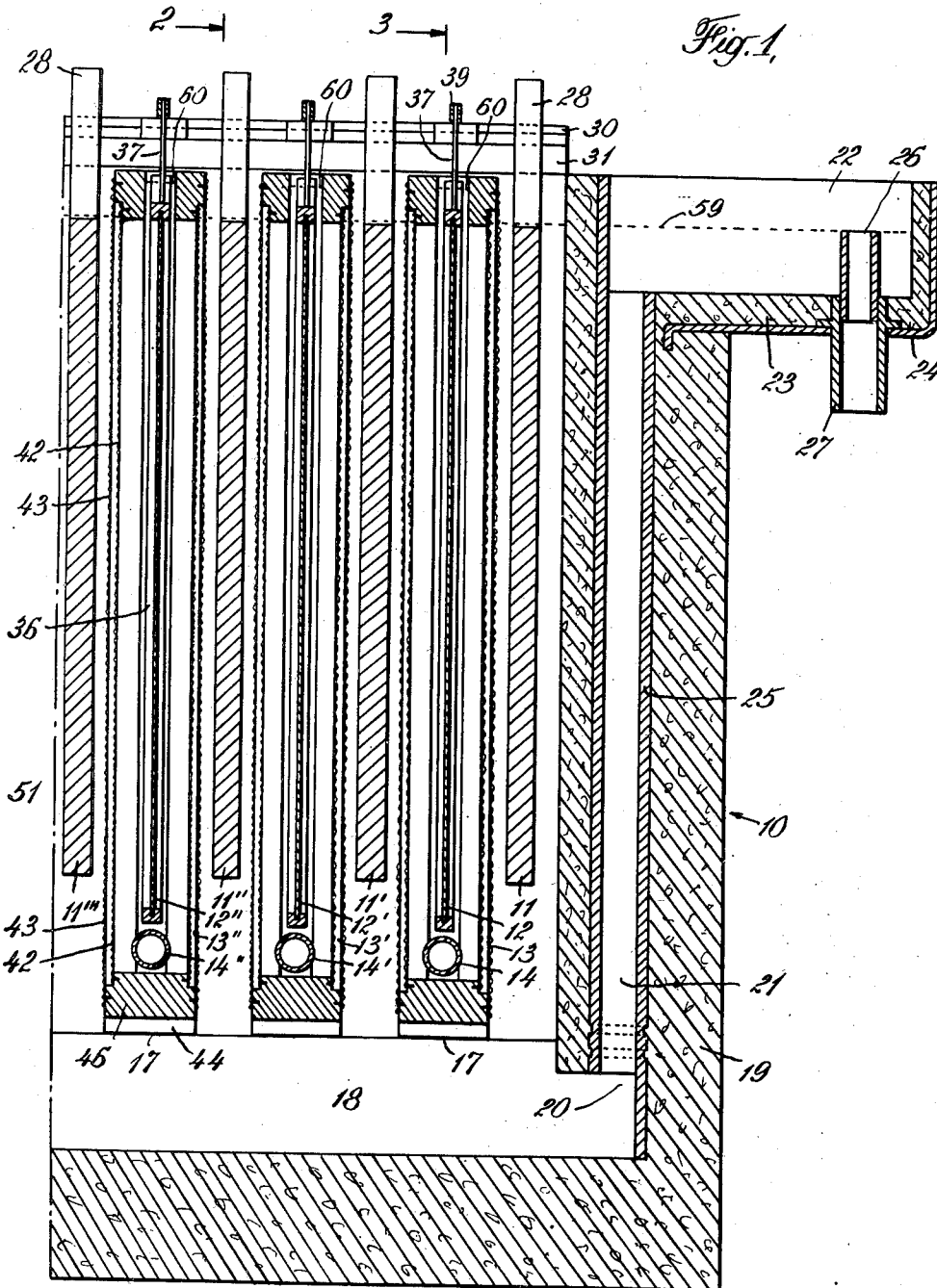
A. M. GRONNINGSÆTER

2,476,189

PRODUCTION OF MALLEABLE AND ANNEALABLE NICKEL

Filed March 8, 1944

3 Sheets-Sheet 1



2-2 3-3

INVENTOR
Anton Martin Gronningsæter
BY
Jennie Davis Marvin Edwards
ATTORNEYS

Aug. 9, 1949.

A. M. GRONNINGSÆTER

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3 Sheets-Sheet 2

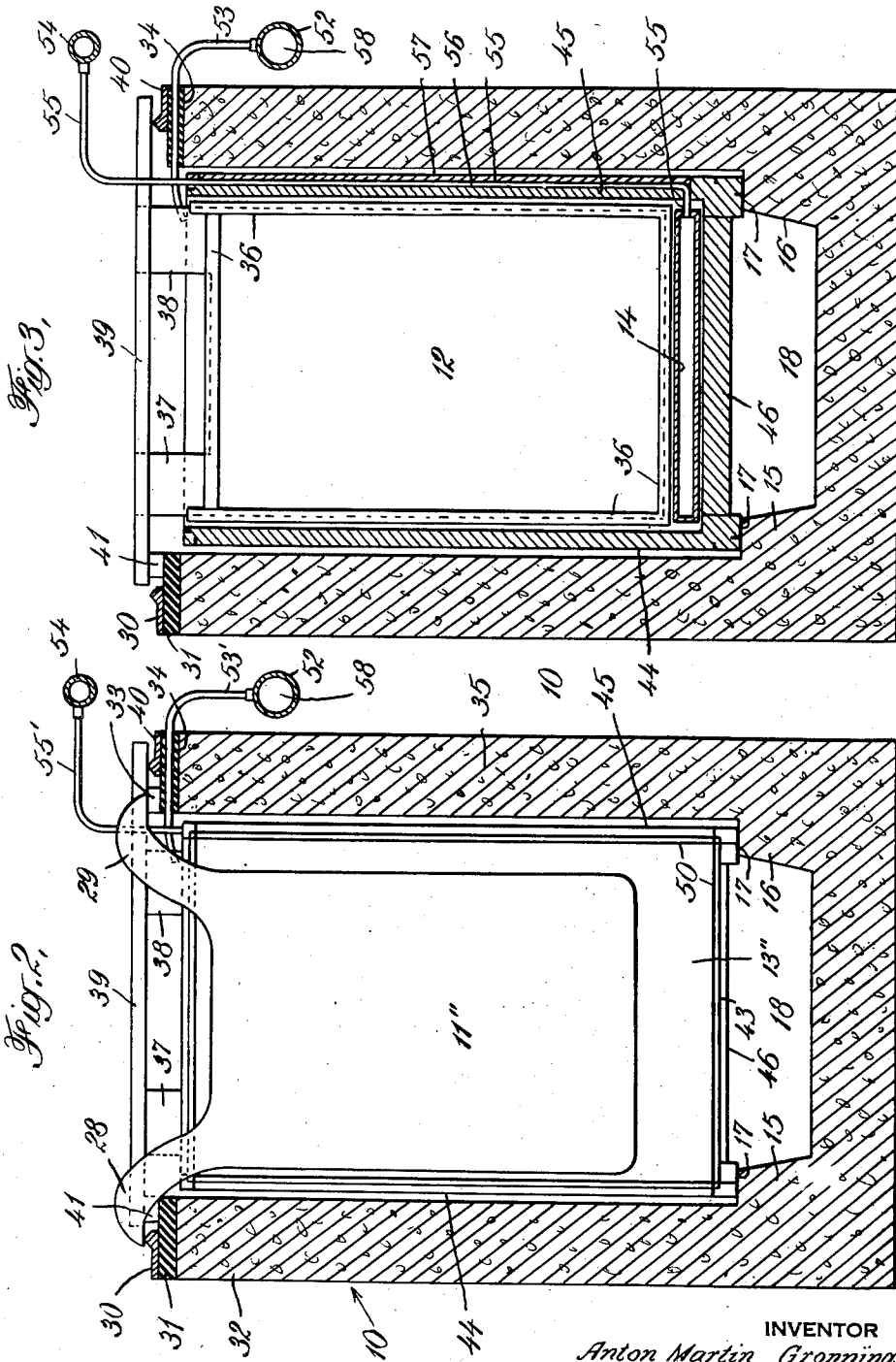


Fig. 3,

Fig. 2,

INVENTOR

Anton Martin Gronningsæter

BY

Pemis, Davis, Merrin, Edmonds
ATTORNEYS

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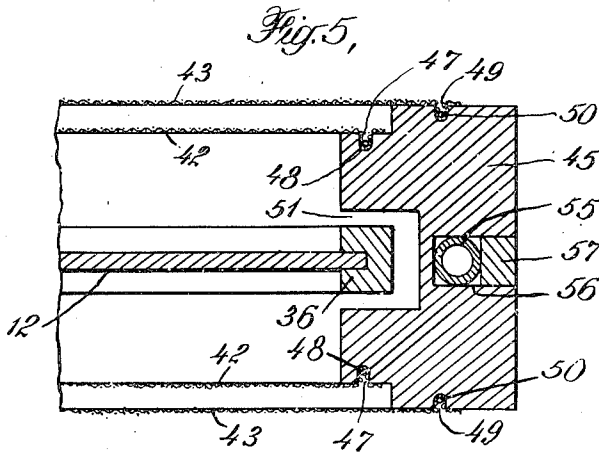
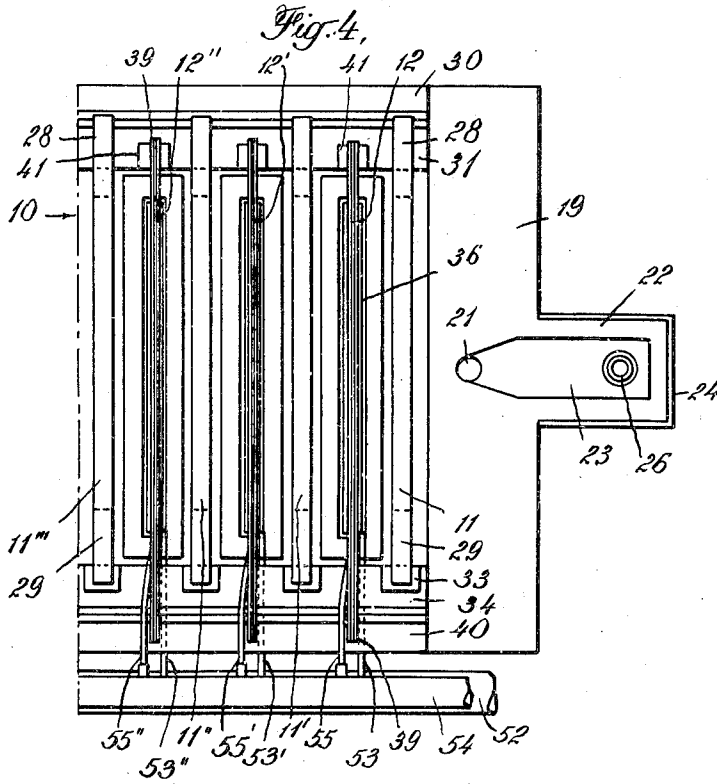
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PRODUCTION OF MALLEABLE AND ANNEALABLE NICKEL

Filed March 8, 1944

3 Sheets-Sheet 3



INVENTOR
Anton Martin Gronningsaeter
BY
Emilia Davis, Marvin Edmunds
ATTORNEYS

UNITED STATES PATENT OFFICE

2,478,189

PRODUCTION OF MALLEABLE AND ANNEALABLE NICKEL

Anton Martin Gronningsaeter, New York, N. Y.,
assignor to Falconbridge Nickel Mines, Limited,
Toronto, Ontario, Canada, a corporation of
Canada

Application March 8, 1944, Serial No. 525,538

4 Claims. (Cl. 204—112)

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This invention relates to the production of malleable and annealable nickel, and has for its object certain improvements in the method of and apparatus for producing malleable and annealable nickel cathodes substantially free of pits and berries in the electrolytic refining of nickel.

Cathodes produced in the electrolytic refining of nickel, that is, primary raw nickel, are frequently malleable but they are often not annealable. That is to say, if the cathodes are annealed in order to soften the nickel, they may become brittle. The problem of producing cathodes directly in nickel refining operations that are both malleable and annealable, and which are substantially free of pits and berries, and which have smooth surfaces, has remained unsolved for many years.

It has been proposed to make nickel sheets ready for rolling or other mechanical treatment by electrolytic deposition. In this connection it has been proposed to melt the nickel and cast it into anodes, which are employed to produce malleable and annealable nickel sheets by electrolytic deposition. This procedure is cumbersome, inconvenient, and expensive.

To make the prior art nickel annealable, it is customary first to melt it. During the melting operation, the nickel takes on oxygen to form nickel oxide; and carbon is usually added to the molten nickel to remove objectionable amounts of the nickel oxide. This operation results in the retention of a certain amount of carbon in the nickel. To condition the nickel properly in this manner requires the careful attention of highly skilled operators.

The carbon-treated molten nickel is then poured into moulds and the resulting ingots are subsequently rolled or otherwise mechanically worked into desired shapes. The mechanical working operation is necessarily divided into a number of steps. The initial ingot is first worked into a smaller shape which is then annealed to remove the brittleness worked into the nickel. After annealing, the nickel is again mechanically worked into a still smaller shape which is then annealed to remove the brittleness caused by the second mechanical working operation. This alternate working and annealing is continued until the final desired shape is obtained. The final shape is generally annealed and pickled. The prior art method of producing desired shapes of malleable and annealable nickel is very cumbersome and costly.

As a result of my investigations, I have discovered that malleable and annealable nickel

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cathodes may be produced by electrolytic deposition directly from electrolytes in nickel refining operations of the Hybinette type, employing a cathode suspended in a porous cathode bag. The nickel cathodes are substantially free of objectionable imperfections, such as pits and berries, and have smooth surfaces.

If the nickel electrolyte is highly purified and slightly acid, a malleable and annealable nickel cathode is obtained, but it usually contains objectionable berries, usually caused by the formation of hydroxides and their adherence to the cathode surface. On the other hand, if the nickel electrolyte is highly purified and strongly acid, a malleable and annealable nickel cathode is obtained, but it usually contains objectionable pits. The use of a high current density increases the tendency to form berries; while the use of a low current density decreases the tendency to form berries. Similarly, if the electrolyte is maintained at a high temperature, the tendency to form hydroxides, and hence berries, is increased. On the other hand, if the electrolyte is maintained at a low temperature, the tendency to form hydroxides, and hence berries, is decreased.

Malleable and annealable nickel cathodes of the desired smoothness and freedom from pits and berries cannot be obtained by the control only of a single one of the variables just mentioned, which go into the electrolytic process of producing nickel cathodes. I have discovered that a suitable compromise of the variables is necessary and that that alone, however, is not sufficient. It is necessary, in addition, to introduce a myriad of minute air bubbles at the bottom of and within the cathode bag along the outside of the cathode. The minute air bubbles moreover must be sufficient in amount to stir the nickel electrolyte next to the cathode so vigorously with surrounding electrolyte in the bag that accumulation of pit- and berry-forming hydrogen gas bubbles and the adherence of berry-forming solid impurities on the cathode are substantially prevented, and to prevent electrolyte next to the cathode from becoming sufficiently basic to form objectionable berry-forming hydroxides on the cathode. In other words there is an optimum operating range for each variable of the process, which without anything more may nevertheless produce a small but objectionable amount of pits and berries, but the formation of which can be avoided by the suitable use of air bubbles.

So far as the nickel electrolyte itself is concerned, it appears that the impurities which work away from the production of malleable and an-

nealable nickel cathodes of the kind described are the impurities which undergo a physical or chemical change during subsequent annealing operations, which are usually conducted at 800°-900° C., and which tend to impair the structure of the nickel. Such impurities as lead, arsenic and organic matter are normally present in nickel electrolyte and tend to remain in the electrolyte. I have discovered that if these impurities are substantially entirely removed, a highly purified electrolyte is obtained which may be used in the practice of the present invention. While the highly purified nickel electrolyte may be prepared in any suitable manner, I have found that when the electrolyte is purified in accordance with the procedures disclosed in my U. S. Patents 1,986,967 of January 8, 1935, 2,066,347 of January 5, 1937, 2,115,019 of April 26, 1938 and my co-pending application Serial No. 297,054 filed September 29, 1939, which has become abandoned, it is highly satisfactory for the purposes of the present invention.

In accordance with the method of the invention, malleable and annealable nickel cathodes substantially free of pits and berries and with smooth surfaces are produced by electrolytic deposition directly from electrolytes in nickel refining operations of the Hybinette type, employing a cathode suspended in a porous cathode bag, by subjecting an acidified highly purified nickel electrolyte containing in excess of 25 grams of nickel per liter with a pH of 1.5 to 4 at a temperature of 40 to 80° C. to electrolysis at a current density of 0.5 to 5 amperes per square decimeter, the electrolyte being substantially free of such impurities as lead, arsenic and organic matter, and introducing a myriad of minute air bubbles within and at the bottom of the cathode bag along the entire width of the cathode, said minute air bubbles being sufficient in amount as they rise along the outside surface of the cathode to stir the nickel electrolyte next to the cathode so vigorously with surrounding electrolyte in the bag as to prevent the adherence of pit- and berry-forming hydrogen gas bubbles and berry-forming solid impurities on the cathode and to prevent electrolyte next to the cathode from becoming sufficiently basic to form objectionable berry-forming impurities on the cathode.

The invention will be better understood by referring to the accompanying drawings, taken in conjunction with the following description, in which:

Fig. 1 is a longitudinal section of an electrolytic cell or deposition tank illustrative of a practice of the invention, showing a series of anodes, cathodes, cathode bags, and air-disseminating members;

Fig. 2 is a cross-section on the line 2—2 of Fig. 1, showing the manner in which the anodes are mounted;

Fig. 3 is a cross-section on the line 3—3 of Fig. 1, showing how the cathodes and air-disseminating members are mounted within the cathode bags, and their position relative to one another;

Fig. 4 is a plan view in part of the cell, showing an electrolyte over-flow extension, for the removal of impure electrolyte, in addition to the anodes, cathode bags and cathodes; and

Fig. 5 is an enlarged sectional transverse view in part, showing the construction of the cathode and cathode bag, in addition to the means for passing air to the air-disseminating member.

Referring first to Figs. 1 and 4, the electrolytic

cell or deposition tank shown comprises: a rectangular tank 10; a series of anodes 11, 11', 11'', 11''', etc.; and a series of cathodes (or cathode starting sheets) 12, 12', 12'', etc., appropriately mounted within cathode bags 13, 13', 13'', etc., respectively, the bottoms of the cathode bags being provided with porous air-disseminating members 14, 14', 14'', etc., respectively, positioned directly underneath the cathodes.

The walls and bottom of the tank are advantageously made of reinforced concrete, the inside surfaces being lined with a protective mastic coating (not shown). The bottom of the tank (see Figs. 2 and 3) is provided with inwardly extending shoulders 15 and 16, the flat upper surfaces 17 of which are adapted to support the cathode bags. The shoulder portions, in addition, define a lower chamber or well portion 18, below the anodes, cathodes, cathode bags and air-disseminating members, for the free circulation of electrolyte.

One end 19 (see Figs. 1 and 4) of the tank is provided at its bottom and center with a lateral passage-way 20 communicating with a vertical passage-way 21, and an outer trough 22, which extends across the top of an over-flow extension member 23, suitably mounted at that end of the tank and supported by a bent metal member 24, attached to the end of the tank. The vertical passage-way 21 is provided with a liner 25 of suitable material, such as mastic or rubber, that is not objectionably reactive with the electrolyte. The over-flow extension member 23 is in turn provided with an adjustable over-flow pipe 26 telescopically fitted into a discharge conduit 27 integrally attached to the extension member. The discharge conduit in turn communicates with other apparatus (not shown) for the treatment of anolyte passed therethrough.

Referring more particularly to Fig. 2, it will be seen that the anodes 11 are provided with laterally extending ears 28 and 29 to provide a support for the suspension of the anodes in the tank. The anodes may be of the soluble, pure or impure, or of the insoluble type. Ear 28 rests upon an anode bus bar 30 (connected to a source of electrical current, not shown) extending lengthwise of the top of the tank, and is in turn supported on an insulation member 31 resting upon side wall 32 of the tank. The other ear 29 rests upon a relatively short piece of insulating material 33, which is in turn supported by an insulation member 34 extending lengthwise of the tank and resting on the top of side wall 35 of the tank.

Referring next to Fig. 3, the cathode, or cathode starting sheet 12 is mounted, as shown, within a frame 36, advantageously constructed of wood, that is adapted to prevent deposition of nickel around the edges or rim of the cathode starting sheet; and thus makes it relatively easy to strip the nickel cathode from the cathode starting sheet. The upper end of the cathode starting sheet is provided with side shoulder portions 37 and 38, to the upper ends of which is attached a lateral cathode support bar 39. One end of the support bar rests upon a cathode bus bar 40 (connected to a source of electrical current, not shown) extending lengthwise of the tank. The bus bar is in turn supported by said insulation member 34. The other end of the cathode support bar rests upon a relatively short piece of insulation 41, supported by said insulation member 31. Each cathode, and cathode starting sheet, is supported within a bag, preferably made of canvas, of the well-known Hybinette type.

If reference is now made to Fig. 5, it will be seen that the instant cathode or Hybinette bag is provided with double side walls consisting of an inner canvas sheet 42 and an outer canvas sheet 43 suitably spaced apart, extending along the two sides of the bag proper, and appropriately mounted on a cathode bag frame consisting of side members 44 and 45, and a bottom member 46, advantageously constructed of wood. The opposite sides of the side members 44 and 45 of the frame are provided with in-set portions (as shown) in which are located vertically disposed grooves 47 into which a juxtaposed portion of the inner canvas sheet 42 is pressed and tightly held in position by means of a suitable string or cord 48 forced into the groove. In a similar manner, the side members of the frame are provided with vertically disposed grooves 49 into which a portion of the outer canvas sheet 43 is pressed and securely tied in position by means of a suitable string or cord 50 forced into the groove.

The side members 44 and 45 of the cathode bag frame are also provided with an open rectangular slot 51 extending vertically and centrally of the interior face to accommodate freely the frame 36 of the cathode starting sheet. The frame is thus held in position, within the slot, and the cathode starting sheet or cathode 12 may be slid into or out of position within the tank.

Referring to Figs. 2, 3 and 4, it is seen that the apparatus illustrated is also provided with an electrolyte distributing pipe 52 extending lengthwise of the tank, near the upper end of side wall 35. A series of branch conduits 53, 53', 53'', etc. connect with the electrolyte distributing pipe, and the free end of each branch conduit extends across the top of the side wall of the tank, and over the open top of a cathode bag.

Figs. 2, 3 and 4 likewise disclose the use of an air distributing pipe 54 extending lengthwise of the tank. A series of branch conduits 55, 55', 55'', etc., preferably made of non-conducting material, such as hard rubber, connect with the air distributing pipe. Each branch conduit extends downwardly through the side member 45 of a cathode bag frame. As shown in Fig. 5, the side member of the cathode bag frame is provided with a vertically and exteriorly disposed slot 56 extending centrally thereof. The branch conduit 55 is held in position within the vertically disposed slot by means of a filler member 57. The lower end of each branch conduit (see Fig. 3) extends laterally from the lower portion of the side member 45 of the cathode bag frame through its inner face, and connects with an air-disseminating member 14, preferably constructed of porous ceramic material, resting on the impermeable bottom member 46 of the cathode bag frame, and directly underneath the cathode or cathode starting sheet 12. The outside diameter of the ceramic tube is advantageously about 2", and its length is about the same as the width of the lower edge of the cathode or cathode starting sheet. As shown, the free end of the tube is closed. The pore sizes of the air-disseminating tube are very small, to assure the formation of minute bubbles.

In operation, a continuous stream of nickel electrolyte 58, such as nickel sulphate, passes through distributing pipe 52 and branch conduits 53, 53', 53'', etc., into cathode bags 13, 13', 13'', etc., until an appropriate electrolyte liquid level 59 is reached within the tank proper. The velocity of the electrolyte in its passage to the electro-deposition tank is so regulated as to main-

tain a cathode bag electrolyte level 60 about 1" higher inside than outside the bags. Electrical current is supplied to the anode and cathode bus bars 30 and 40, as a result of which the conventional electrolysis step takes place, nickel being deposited on the cathode or cathode starting sheets 12, 12', 12'', etc., as the anodes 11, 11', 11'', etc. go into solution, if the soluble type of anode is employed. The resulting anolyte (impure nickel electrolyte) passes down into well 18, through passage 20, up passageway 21, laterally across trough 22, and down over-flow pipe 26 to be enriched in nickel, purified, and re-cycled to the tank for further electrolytic treatment.

The electrolyte used is preferably the same as that generally used for the production of ordinary cathode nickel, except that it is highly purified, as pointed out above, and its acidity is advantageously increased, for example, by the addition of sulphuric acid; so that the pH value of the electrolyte will be below 4, preferably between 1.5 and 3.5. The concentration of nickel in the electrolyte should be in excess of about 25 grams per liter. The temperature of the electrolyte entering the cathode bags is kept between 40° C. and 80° C. preferably between 50° C. and 70° C. The current density used for deposition may be varied within 0.5 and 5 amperes per sq. dm., but is preferably between 1 and 2 amperes per sq. dm.

In a specific example of the invention, nickel sulphate electrolyte containing about 50 grams of nickel per liter, 20-25 grams of sodium sulphate per liter and 25 grams of boric acid per liter was employed. The electrolyte had a pH of about 5.5 as it came from the cementation and neutralization operation and a pH of about 3.5 as it went into the electrolytic cell. The electrolyte had a temperature of about 55 C. as it went into the cell and was subjected to electrolysis at a current density of about 1.3 amperes per square decimeter. The concentration of nickel in the electrolyte was in excess of 25 grams per liter.

The nickel is deposited on starting sheets or mother plates 12 of suitable material, such as aluminum or stainless steel. The starting sheets are provided with a frame 36 to prevent the nickel from growing around the edges of the mother plates. When the nickel cathodes have grown to the desired thickness, for instance, 4-5 mms., the nickel is separated from the mother plates, and is then ready for mechanical working, while the mother plates are again used for the deposition of further nickel cathodes.

A supply of air under appropriate pressure is continuously passed through distributing pipe 54, and branch conduits 55, 55', 55'', etc., into and through the porous ceramic air-disseminating members 14, 14', 14'', etc. The supply of air is so regulated as to cause the resulting air bubbles to be well dispersed throughout the electrolyte surrounding the cathodes or starting sheets, without excessive foaming.

The use of air bubbles in the manner described offers a number of important advantages. The bubbles, in conjunction with the electrolyte, clean, sweep or wash the cathode or starting sheet surfaces free of deposited berry-forming impurities; and scour off hydrogen bubbles which attach themselves to the surface, and which would, therefore, form pits unless removed.

Conditions at the cathode surfaces are always in flux, and they are not the same as elsewhere in the body of electrolyte. For example, even with an acidic nickel-sulphate electrolyte, condi-

tions tend to become basic at the cathode surface. The sulphuric acid present in the electrolyte dissociates into sulphate anions and hydrogen cations. The former migrate through the bag to the anode, while the latter migrate to the cathode, where they are discharged, resulting in the liberation of hydrogen gas. In the thin film of electrolyte next to the cathode, from which deposition of the nickel takes place, hydrogen ions are as a rule discharged so quickly that migration of new hydrogen ions into the film cannot keep step, which results in a material decrease in the concentration of hydrogen ions in the electrolyte adjacent the cathode; this means that the acidity decreases, or, what is the same, the pH value rises. Even when the main body of the electrolyte remains acidic, the film next to the cathode can be so much depleted in hydrogen ions that traces of hydroxides or basic salts are formed. These hydroxides tend to adhere to the cathode, and thus form nuclei for the formation of berries. The presence of foreign solid particles on the cathode surface is also known in many cases to be responsible for hydrogen bubbles sticking to the surface, which will result in pits.

In accordance with the present invention, however, the action of the moving air bubbles is to stir the electrolyte next to the cathodes so vigorously with surrounding electrolyte as to inhibit the tendency of any of it to become basic, thus at the same time inhibiting the formation of hydroxides. At the same time, if slime particles consisting of hydroxides or the like should be formed and be moved onto the cathodes, the action of the moving air bubbles is promptly to sweep them away and to keep the cathodes clean.

As a result of the breaking up of the acid at the cathodes during electrolysis, hydrogen is released which normally tends to accumulate on the cathodes in the form of minute bubbles, where it will be responsible for the formation of pits. In accordance with the invention, however, the moving air bubbles tend to loosen the hydrogen bubbles from the cathodes, and such hydrogen as does contact the cathodes is promptly brushed or swept away by the air bubbles and agitated electrolyte, thus avoiding the collection of pit- and berry-forming nuclei on the cathode surfaces.

This application is a continuation-in-part of my application Serial No. 284,045, filed July 12, 1939, which has become abandoned.

I claim:

1. In the method of producing malleable and annealable nickel cathodes substantially free of pits and berries and with smooth surfaces by electrolytic deposition directly from electrolytes

in nickel refining operations of the Hybinette type employing a cathode suspended in a porous cathode bag, the steps which comprise subjecting an acidified highly purified aqueous nickel plating electrolyte containing in excess of 25 grams of nickel per liter with a pH of 1.5 to 4 at a temperature of 40 to 80° C. to electrolysis at a current density of 0.5 to 5 amperes per square decimeter, said electrolyte being substantially free of lead, arsenic and organic matter, and introducing a myriad of minute air bubbles within and at the bottom of the cathode bag along the entire width of the cathode, said minute air bubbles being sufficient in amount as they rise along the surface of the cathode to stir the nickel electrolyte next to the cathode so vigorously with surrounding electrolyte in the bag as to prevent the adherence of pit- and berry-forming hydrogen gas bubbles and berry-forming solid impurities on the cathode and to prevent the electrolyte next to the cathode from becoming sufficiently basic to form objectionable berry-forming impurities on the cathode.

2. Method according to the preceding claim, in which the nickel electrolyte has a pH value of 1.5 to 3.5 and a temperature of 50 to 70° C., and a current density of 1 to 2 amperes per square decimeter is employed.

3. Method according to claim 1 in which the electrolyte is nickel sulfate.

4. Method according to claim 2 in which the electrolyte is nickel sulfate.

ANTON MARTIN GRONNINGSÆTER.

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