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A. M. GRÖNNINGSAETER
PRODUCTION OF NICKEL BY ELECTROLYTIC DEPOSITION
FROM NICKEL SALT SOLUTIONS
Filed Aug. 15, 1933

2,066,347

2 Sheets-Sheet 1

Fig. 1.

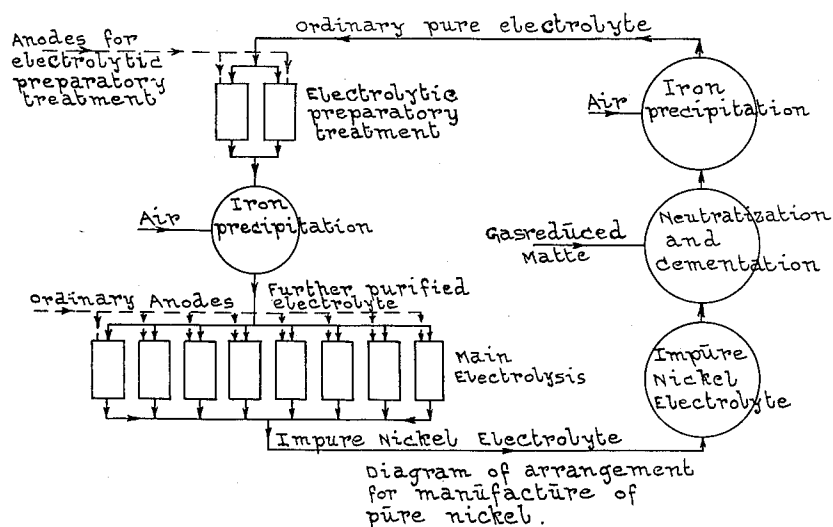


Fig. 2.

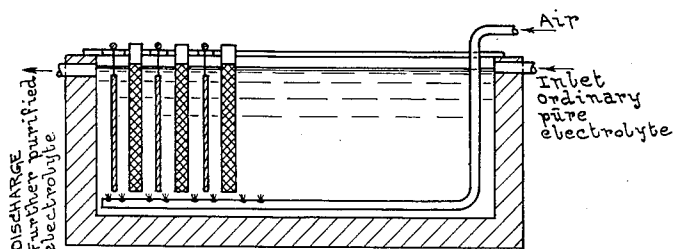


Fig. 3.

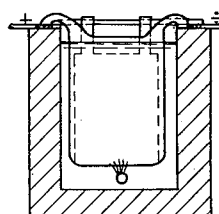
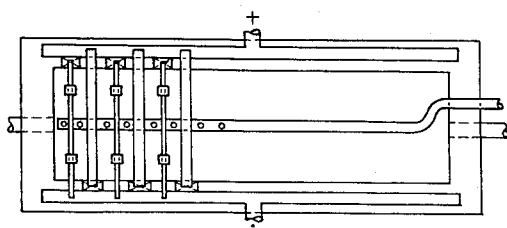


Fig. 4.



Arrangement of tank for use of pure soluble nickel anodes.

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2 Sheets-Sheet 2

Fig. 5.

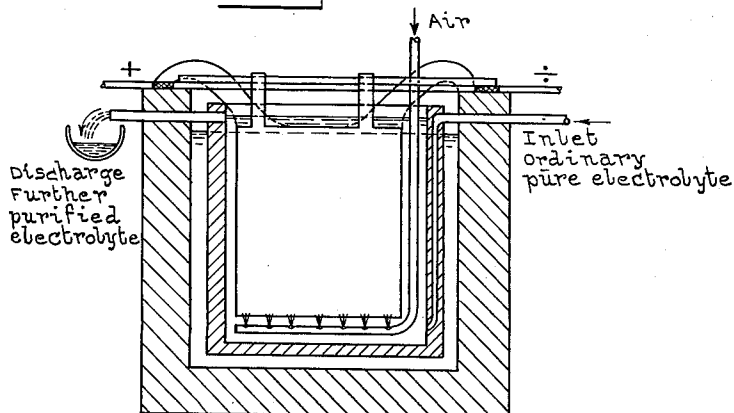
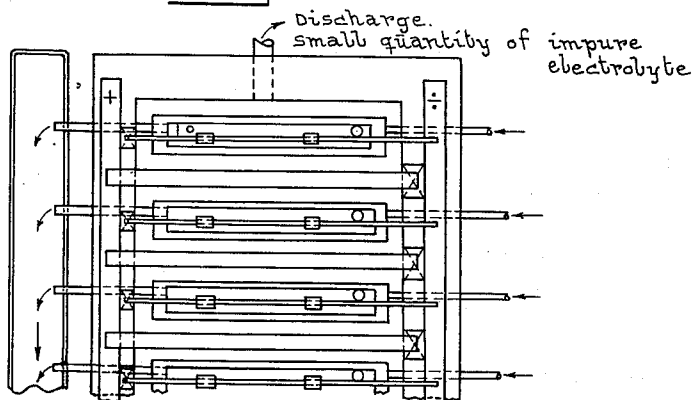


Fig. 6.



Arrangement of tank for use of
insoluble anodes or impure nickel Anodes.

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UNITED STATES PATENT OFFICE

2,066,347

PRODUCTION OF NICKEL BY ELECTROLYTIC
DEPOSITION FROM NICKEL SALT SOLUTIONS

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Application August 15, 1933, Serial No. 685,226
In Norway September 3, 1932

10 Claims. (Cl. 204—57)

This invention relates to the production of nickel by electrolytic deposition from nickel salt solutions and has for its object a process of preparing solutions for such electrolysis.

5 In the electrolytic production of nickel, for example by the well known Hybinette process in connection with the use of anodes containing copper, iron and other impurities, the purification of the electrolyte is effected in various ways, 10 for example by means of a process already invented by the applicant (U. S. patent application Serial No. 487,369, which has since issued into Patent 1,986,967) according to which the electrolyte is freed from copper by cementation and at the same time neutralized by means of 15 gas-reduced nickel, the iron being removed by subsequent blowing with air.

In this manner it has been made possible to produce an electrolyte of a high degree of purity, by means of which a very pure nickel is produced. 20

However, the methods hitherto employed for the purification of nickel electrolytes have not resulted in a nickel of a higher degree of purity than as to still contain some hundredths percents 25 of foreign elements.

When the term nickel is made use of in this connection without expressly mentioning cobalt, the expression is meant to comprise nickel containing also small percentages of cobalt, which 30 usually is not considered as an impurity and which, when present in small quantities, ordinarily does not exert any appreciable influence, although such possible influence is advantageous in its tendency.

35 The present invention has for its object a process by which it is made possible to obtain a purer nickel than that which has hitherto been produced on a commercial scale. This process utilizes the relative position of the elements in the electrochemical series as well as their electrochemical behaviour in other respects as overvoltages and mobilities of the ions. When an electrolyte has been purified in the ordinary way it still contains small quantities of foreign elements, 40 such as copper, iron, arsenic and lead. The electrochemical relations of these elements are such as to make it seem probable that they under suitable conditions would be deposited more readily than nickel in the course of electrolysis. Experiments have now shown this to be the case, 45 and the invention has for its object to subject an electrolyte, which has been purified in the usual manner, to an electrolytic preparatory treatment, conducted in a special way, whereby the said impurities or a considerable proportion of same are 55

deposited together with a comparatively small proportion of the total nickel. In the nickel so obtained the impurities are concentrated (for example to five to twenty times the percentage of impurities contained in nickel produced from the same electrolyte when no preparatory treatment 5 is employed). This comparatively impure nickel may, if desired, be returned to a prior stage of the process.

By these means a further purified electrolyte 10 is obtained, which is thereupon subjected to electrolysis in ordinary electrolytic cells for the deposition of nickel.

In the modern electrolytic refining of nickel it is necessary to keep the acidity of the electrolyte 15 under accurate control, and the removal of impurities above referred to must take place in such a manner that the pH of the electrolyte can be maintained within definite limits. The purification treatment therefore must be so arranged as 20 to avoid the liberation or introduction of substantial proportions of free acid in the electrolyte and, at the same time so as to prevent the introduction of considerable amounts of impurities from the anodes into the electrolyte. These conditions may be complied with in several ways. 25

One way of obtaining such purification involves the use of soluble nickel anodes which do not contain substantial quantities of foreign metals. 30

Pure nickel anodes with a sufficient high degree of solubility can be produced by known methods, for example by introducing nickel oxide or carbon into the anodes. This has been found to increase the solubility of the anodes to a very 35 high degree. The anodic solubility of such anodes is influenced by the current density in such manner that the solubility will decrease when too high current densities are employed. A suitable current density is for instance about 10 40 amperes per sq. ft. By the use of such anodes no liberation of free acid will take place because approximate balance between deposited and dissolved metal will be established. It is even possible by the use of anodes of sufficient solubility 45 in connection with regulation of the current density employed to bring about an increase of the pH of the electrolyte in the course of its passage through the cell in which the preparatory treatment is taking place. 50

By a preparatory treatment conducted in this manner simple cells without partitions between anodes and cathodes may be employed.

The construction and arrangement of these cells may be carried out in various ways. A 55

certain number of ordinary electrolytic tanks may be used. Or tanks of greater length but fewer in number may be employed. The flow through the purifying tanks may be arranged in parallel or in series or as a combination of both, etc.—In practice it will in most instances be convenient to employ the ordinary type of deposition tanks. In carrying out the preparatory treatment it is important to bring the electrolyte into the best possible contact with the cathodes. This can be brought about by violent agitation and mixing of the electrolyte, for example by means of air and by having a large cathode surface in relation to the quantity of electrolyte flowing through the tanks. The last named condition may be established by arranging the greatest possible number of anodes and cathodes in each tank.

By the use of simple cells without separating anodes and cathodes a great number of electrodes may be placed in each tank, and as a consequence of this a flow of a great volume of electrolyte through each tank may be maintained. The number of tanks for the preparatory treatment can therefore be small as compared with the number of the tanks for the main electrolysis. For this reason low capital costs are required for the plant needed to carry the process into effect.

In the example above mentioned it is presumed that soluble pure nickel anodes are used in the preparatory treatment.

In another alternative method of carrying the treatment into effect one may use insoluble or poorly soluble anodes or anodes containing impurities, for example such as the previously mentioned ordinary anodes employed in the Hybinettes process. But in this case the anode and cathode compartments must be separated so that appreciable amounts of impurities and free acid cannot enter into the cathode compartment from the anode compartment. The cathode may, for example be surrounded by an ordinary Hybinette-bag, into which a much larger quantity of electrolyte is passed than that which passes through the bag walls.

An overflow of electrolyte is thus produced, which on passing the cathode has been freed from a considerable proportion of its contents of foreign metals. In the cathode chamber agitation of the electrolyte may be provided for example by blowing air into the same.

During the passage of the electrolyte through the cathode compartment, no acid becomes liberated. On the contrary a decomposition of acid may take place so that an increase of the pH of the electrolyte may result.

If the comparatively impure nickel, produced by one of these methods, is going to be returned to the system, it is of importance to keep the quantity of same in proportion to the total nickel as low as possible, and with this in view the current density during the preparatory electrolytic treatment should be kept as low as the demands for sufficient purification will permit.

By purification of the electrolyte according to these methods most of the copper, arsenic and lead can be removed. Iron and cobalt however, cannot be removed with the same degree of completion, and in order to produce a nickel with a particularly low percentage of these two metals special additional treatments are required.

It is known that iron can be precipitated from nickel solutions having a sufficiently high pH-

value by means of oxydation for example by blowing with air. Such precipitation is promoted by high pH-values.

In the methods of preparatory electrolytical treatments above described, it is possible to maintain a high pH in the electrolyte and also if desired to raise the pH value. It being thus possible to obtain suitable conditions of operation, precipitation of iron may be combined with the preparatory electrolytical treatment. The electrolyte is then after the preparatory electrolytic treatment subjected to an oxydizing treatment, for instance the action of air; the iron is then oxydized, and is precipitated due to hydrolysis. By means of this repeated treatment the iron is removed down to minute traces.

It is also possible when such steps for the removal of iron is taken after the preparatory electrolytic treatment, to omit the steps for iron removal in the preceding process. The electrolyte is then only treated with gas-reduced nickel, in order to remove the copper and neutralize the acid, and is then directly afterwards led through the preparatory electrolytic treatment, after which the electrolyte is subjected to an oxydizing treatment in order to precipitate the iron present.

As the increase of the pH-value obtainable by the preparatory electrolytic treatment is influenced by the pH of the electrolyte during said treatment, it is in some cases desirable partly to precipitate the iron prior to the electrolytic treatment. The pH will then decrease with an amount that is in proportion to the quantity of iron precipitated.

During the preparatory electrolytic treatment the pH again will increase, and thereby conditions for a complete removal of iron are obtained. In this case the electrolyte is at first subjected to an oxydizing treatment, whereby for instance $\frac{2}{3}$ of the total quantity of iron is precipitated, the electrolyte is then—without first removing the precipitate—led through the preparatory electrolytic treatment, and afterwards the remaining iron is precipitated by action of air or by other chemical methods.

After finished purifying treatments the electrolyte may be subjected to filtration and if necessary its pH may be adjusted before it enters into the ordinary electrolytic system.

It has been found to be possible by the means above described to produce with small extra costs a nickel of higher purity than that which has hitherto been on the market.

In an electrolytic preparatory treatment conducted as above indicated, cobalt will also be concentrated in the impure nickel. But in view of the fact that the percentage of cobalt present in the nickel electrolyte subjected to the preparatory electrolytic treatment is much higher than that of the other foreign metals, the deposited quantity of cobalt will represent only a fraction of the entire quantity of cobalt in the solution.

In case it for some reason is desired to decrease the amount of cobalt in the electrolytically produced pure nickel, or if it is wanted to utilize more or less of the contents of cobalt in the electrolyte, it is possible by means of suitable working conditions, such as rapid flow of the electrolyte, low current density, rotating cathodes or the like, to deposit a greater quantity of the cobalt, and thus an impure nickel with a higher content of cobalt is obtained.

The electrolyte, after being purified from copper, arsenic, lead etc. by the previously de-

scribed treatment, may also be subjected to a special electrolytic treatment under the same above mentioned working conditions, which facilitate the deposition of cobalt, and in this way it is possible to obtain a pure nickel with such a high percentage of cobalt that the metal may have a special value owing to its cobalt contents.

To illustrate what is obtained by the process according to the invention the following example is given:

Nickel produced without preparatory treatment:

	Per cent
Co	0.7
Cu	0.01
As	0.005
Pb	0.005
Fe	0.01

Impure nickel from preparatory treatment:

	Per cent
Co	3.0
Cu	0.15
As	0.06
Pb	0.05
Fe	0.01

Pure nickel from main electrolysis after preparatory treatment:

	Per cent
Co	0.6
Cu	0.002
As	0.002
Pb	0.002
Fe	0.002

In the accompanying drawings the embodiments of the invention above described are diagrammatically illustrated.

Fig. 1 is a flow sheet, indicating the successive steps herein described in the manufacture of nickel;

Fig. 2 is a side elevation in section of an electrolytic cell employable for the preliminary or preparatory electrolysis step;

Fig. 3 is an end elevation in section through the cell of Fig. 2;

Fig. 4 is a plan view of the cell of Fig. 2;

Figs. 5 and 6 are views of an electrolytic tank particularly adapted for the use of insoluble anodes or impure nickel anodes.

I claim:

1. The improvement in the production of nickel by electrodeposition which comprises first subjecting an impure nickel electrolyte contaminated with an objectionable amount of copper, iron, arsenic, lead and the like to copper cementation on gas-reduced nickel and to iron precipitation by oxidation to remove the bulk of the copper and iron and to render the electrolyte substantially neutral, then subjecting the electrolyte still slightly contaminated with a small quantity of at least one of said impurities to at least one preliminary electrolysis step conducted in the presence of a soluble nickel anode that is substantially free from foreign metals to prevent a substantial increase in the acidity of the electrolyte during which relative movement is rapidly effected between the electrolyte and the cathode and the impurities are promptly and frequently brought into contact with the cathode to deposit a relatively small portion of the nickel and a relatively large amount of said impurities on the cathode, whereby an impure nickel product of low grade is obtained, and then subjecting the nickel electrolyte thus purified to a separate and

main electrolysis operation of the conventional type to effect the deposition of a relatively large amount of the nickel substantially free of said impurities, whereby a nickel product of high purity is obtained.

2. A process according to claim 1, in which the preliminary electrolysis step is conducted in the presence of soluble nickel anodes, and adjusting the rise in the pH value of the electrolyte during the preliminary electrolysis step by varying the current density and the total current employed in proportion to the flow of electrolyte through the cell so as to effect neutralization of the electrolyte to such a degree that iron present may be substantially completely precipitated by oxidation and hydrolysis.

3. A process according to claim 1, in which the electrolyte is thoroughly aerated to precipitate iron before the electrolyte is subjected to said preliminary electrolysis step.

4. A process according to claim 1, in which the electrolyte is thoroughly aerated to precipitate iron after the preliminary electrolysis and before the main electrolysis steps.

5. A process according to claim 1, in which the electrolyte is thoroughly aerated before, during and after the preliminary electrolysis step to precipitate iron.

6. The improvement in the method of effecting the electrodeposition of nickel which comprises first subjecting a substantially neutral nickel electrolyte containing an appreciable amount of cobalt in solution to at least one preliminary electrolysis step conducted in the presence of a soluble nickel anode that is substantially free from foreign metals to prevent a substantial increase in the acidity of the electrolyte while relative movement is rapidly effected between the electrolyte and cathode to deposit a portion of the nickel high in cobalt, and then subjecting the nickel electrolyte thus partially freed of cobalt to a main electrolysis operation to effect the deposition of nickel relatively low in cobalt.

7. The improvement in the method of effecting the electrodeposition of nickel which comprises first subjecting a substantially neutral nickel electrolyte containing an appreciable amount of cobalt in solution to at least one preliminary electrolysis step conducted in the presence of a soluble nickel anode that is substantially free from foreign metals to prevent a substantial increase in the acidity of the electrolyte under a low current density to deposit a portion of the nickel high in cobalt, and then subjecting the nickel electrolyte thus partially freed of cobalt to a main electrolysis operation to effect the deposition of nickel relatively low in cobalt.

8. The improvement in the production of nickel by electrodeposition which comprises first subjecting a substantially neutral nickel electrolyte containing a substantial amount of cobalt in solution and contaminated with a small quantity of at least one metal impurity in the group: copper, arsenic, lead, and the like, to a preliminary electrolysis step conducted in the presence of a soluble nickel anode that is substantially free from foreign metals to prevent a substantial increase in the acidity of the electrolyte during which relative movement is rapidly effected between the electrolyte and the cathode and the impurities are promptly and frequently brought into contact with the cathode to deposit a relatively small portion of the nickel and a relatively large amount of said impurities on the

- cathode, whereby an impure nickel of low grade containing said impurities and some of the cobalt is obtained, and then subjecting the nickel electrolyte thus purified to at least one more preliminary electrolysis step under substantially similar conditions of rapid relative movement between the electrolyte and the cathode to effect the deposition of a comparatively small amount of high purity nickel high in cobalt.
9. A process according to the preceding claim, in which the nickel electrolyte remaining after said preliminary electrolysis steps is subjected to a separate and main electrolysis operation of the conventional type to effect the deposition of high purity nickel comparatively low in cobalt.
10. The improvement in the production of nickel by electrodeposition which comprises first subjecting a substantially neutral nickel electrolyte contaminated with a small quantity of at least one metal impurity in the group: copper, arsenic, lead, and the like, to at least one preliminary electrolysis step conducted in the presence of an impure nickel anode in an electrolytic cell having the anode compartment separated from the cathode compartment by a Hybinette bag that surrounds the cathode, maintaining the electrolyte under an appropriate hydrostatic head so that more electrolyte is passed into said bag than can filter through the same during which relative movement is rapidly effected between the electrolyte and the cathode and the impurities are promptly and frequently brought into contact with the cathode to deposit a relatively small portion of the nickel and a relatively large amount of said impurities on the cathode, whereby an impure nickel of low grade is obtained, and then subjecting the overflow of nickel electrolyte from the Hybinette bag thus purified to a separate and main electrolysis operation of the conventional type to effect the deposition of a relatively large amount of the nickel substantially free of said impurities, whereby a nickel of high purity is obtained.

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