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(54) Titre : UNE METHODE DE PRODUCTION D'HYDROXYDES DE NICKEL PUR ET UTILISATION

(54) Title: A PROCESS FOR THE PRODUCTION OF PURE NICKEL HYDROXIDE AND ITS USE

(57) **Abrégé/Abstract:**

The invention relates to a process for the production of pure nickel hydroxide by anodic oxidation of metallic nickel in aqueous electrolyte solution in the presence of sulfate ions and removal of the nickel hydroxide formed and to the use of the nickel hydroxide thus produced.



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**A PROCESS FOR THE PRODUCTION OF PURE NICKEL HYDROXIDE
AND ITS USE**

A b s t r a c t

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A PROCESS FOR THE PRODUCTION OF PURE NICKEL HYDROXIDE AND ITS USE

This invention relates to a process for the production of pure nickel hydroxide by anodic oxidation of metallic nickel in aqueous electrolyte solution in the presence of sulfate ions and removal of the nickel hydroxide formed and to the use of the nickel hydroxide thus produced.

BACKGROUND OF THE INVENTION

Nickel hydroxide is normally obtained by the reaction of nickel salts with alkali metal hydroxides. The nickel starting solutions are obtained in a first stage by digestion of metallic nickel, for example with HNO_3 . The hydroxide is obtained in a second stage by subsequent precipitation with alkali metal hydroxides. The disadvantages of these processes are, on the one hand, the poor filterability of the nickel hydroxide gel formed. The neutral salts formed and the excess alkali metal hydroxide are also very difficult to remove from the precipitate. Non-stoichiometric basic nickel salts are precipitated in particular from nickel chloride and/or sulfate solutions and are obstacles to conversion into pure hydroxide. In addition, stoichiometric quantities of neutral salts are unavoidably formed in the hydroxide precipitation step and have to be disposed of through the wastewater.

The electrolytic preparation of pure nickel hydroxide from metallic nickel in aqueous solutions of alkali metal salts is described in Italian patent 366 495 issued December 29, 1938. The unwanted formation of basic salts is mentioned in this document, too, and is counteracted by elaborate and hence uneconomical equipment-related measures.

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The formulation of nickel hydroxide in electrolytic processes has also been repeatedly observed as a secondary reaction and is described, for example, by S. C. Real, M. R. Barbosa, J. R. Vilche, and A. J. Arvia in
5 Influence of Chloride Concentration on the Active Dissolution and Passivation of Nickel Electrodes in Acid Sulfate Solutions, J. Electrochem. Soc., Vol. 137, No. 6, 1990, pages 1696 to 1702. According to this reference, the anodic formation of an $\text{Ni}(\text{OH})_2$ layer on nickel electrodes
10 was observed in voltametric measurements in sulfuric acid sulfate electrolyte solutions containing potassium chloride. The experimental results in this reference provide no indication as to how pure nickel hydroxide can be electrochemically produced on an industrial scale.

15 SUMMARY OF THE INVENTION

It has now surprisingly been found that the anodic oxidation of metallic nickel in aqueous electrolyte solutions containing both sulfate and chloride leads to a nickel hydroxide intermediate product which may be
20 economically converted into pure nickel hydroxide by treatment with alkali metal hydroxides.

Accordingly, the present invention relates to a process for the production of pure nickel hydroxide by anodic oxidation of metallic nickel in aqueous electrolyte
25 solution in the presence of sulfate ions and removal of the nickel hydroxide formed, characterized in that a nickel hydroxide containing chloride and sulfate is first prepared and then converted into pure nickel hydroxide by aftertreatment with alkali metal hydroxides.

30 The process according to the invention may advantageously be carried out with low concentrations of

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sulfate and chloride ions. Thus, the concentration of sulfate ions is preferably 0.001 to 2.0 molar and, more preferably, 0.01 to 1.0 molar. The preferred concentration of chloride ions is 0.3 to 5 molar and, more preferably, 0.5 to 2 molar. Particularly good results are obtained if the electrolyte solution contains an excess of chloride ions over sulfate ions. The molar ratio of chloride ions to sulfate ions is 200:1 to 1:1 and, more preferably, 100:1 to 10:1.

10 The process according to the invention is preferably carried out at pH values of 6 to 13 and, more preferably, at pH values of 8 to 12. At lower pH values, the nickel hydroxide is dissolved whereas, at very high pH values, there is normally no formation of basic salts.

15 Instead, a firmly adhering nickel hydroxide can be formed on the anode under these conditions, interfering with the flow of current in the electrolysis cell. In addition, a homogeneous reproducible product cannot be obtained in this way.

20 In one aspect, the invention provides a process for the production of substantially pure nickel hydroxide, comprising the steps of:

(a) providing a metallic nickel source material in an aqueous electrolyte solution comprising sulfate ions and chloride ions, wherein the concentration of sulfate ions is in the range of 0.001 to 2.0 molar and the concentration of chloride ions is in the range of 0.3 to 5 molar, and wherein the molar ratio of chloride to sulfate ions is in the range of from 200:1 to 1:1;

30 (b) conducting a substantially continuous anodic oxidation of the nickel in the aqueous electrolyte solution

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to form nickel hydroxide, while maintaining said concentrations of sulfate and chloride ions and said molar ratio of chloride and sulfate ions, and maintaining a pH of 6 to 13 in the aqueous electrolyte solution, and removing
5 formed nickel hydroxide from the aqueous electrolyte solution;

(c) treating the nickel hydroxide from step (b) by exposure, in a post-anodic treatment solution, to an alkali metal hydroxide at a concentration of 10^{-3} to 2 molar for a
10 period of 1 to 48 hours at a temperature of 20 to 80°C and at an elevated pH compared to the pH of the aqueous electrolyte solution; and

(d) filtering and drying the product of step (c) to thereby obtain a substantially pure nickel hydroxide product
15 with high density, high surface area and a high degree of crystallinity.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In a particularly preferred embodiment of the process according to the invention, the chloride and sulfate
20 ions are introduced in the form of alkali metal

and/or nickel salts. These salts may advantageously be circulated throughout the entire production process.

5 In cases where the pure nickel hydroxide according to the invention is intended to contain doping elements, as is sometimes required of nickel hydroxide for the production of batteries, the process according to the invention may advantageously be carried out in the presence of cadmium, cobalt, magnesium, calcium and/or zinc salts preferably used as sulfate and/or chloride salts. The maximum content of these elements is 10% of the $\text{Ni}(\text{OH})_2$.

10 In another advantageous embodiment, the pure nickel hydroxide may be prepared in the presence of cadmium, cobalt, magnesium and/or zinc, these elements serving as metal anodes.

Good yields are achieved with current densities of approx. 500 to 2000 A/m^2 .

15 The main product obtainable by the process according to the invention is a gel of very high water content (approx. 90% H_2O) which readily lends itself to filtration. The filtrate may advantageously be returned as electrolyte to the electrolysis cell.

20 This main product still contains a few percent chloride and sulfate, although they may readily be removed in the alkaline aftertreatment. The alkali metal hydroxides used are preferably potassium and/or sodium hydroxides in a concentration of 10^{-3} to 2 molar and preferably in a concentration of 10^{-2} to 0.5 molar, the alkali metal hydroxide required advantageously being circulated.

25 The aftertreatment according to the invention may be carried out particularly economically over periods of 1 to 48 hours at temperatures of 20 to 80°C.

30 In the overall balance, therefore, only that quantity of neutral salt which is present as an impurity in the nickel hydroxide is discharged into the wastewater. Compared with conventional processes for the production of nickel hydroxide by precipitation from nickel salts, the electrochemical production process according to the invention represents a reduction in the neutral salt occurrence of at least 90%. The process according to the invention is particularly easy to carry out because it does not involve the use of membranes or diaphragms.

35 The pure nickel hydroxide produced in accordance with the invention ideally fulfills the requirements which an anode material for nickel/cadmium and/or nickel hydride batteries is expected to satisfy. It has a high apparent density and tamped density so that a high volume-specific storage capacity can be achieved in the battery. In addition, anionic impurities which can have an adverse

effect on the electrochemical properties of the batteries are only present in very low concentrations of preferably below 0.2%. Other physical characteristics are, for example, a high specific surface of the nickel hydroxide and a high half-intensity width of the 101 X-ray diffraction reflex of the nickel hydroxide which provides information on the degree of crystallization. The particle sizes are in the range of 1 to 250 μm .

Accordingly, the present invention also relates to the use of the nickel hydroxide produced in accordance with the invention as an anode material in nickel/ cadmium batteries and/or nickel hydride batteries.

The following Examples are intended to illustrate the invention without limiting it in any way.

Comparison Example

15 g NaCl and 1 g $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ were dissolved in 300 ml water. Electrolysis was then carried out with stirring at room temperature at 4 volts and at a current density of 1200 A/m². A rapidly sedimenting gel was formed; after treatment with NaOH (pH 13.5), the gel gave a nickel hydroxide product containing 0.4% chloride.

20 Example 1

a) Electrolysis

An electrolysis reactor consisting of an electrolysis cell (70 l) was filled with 200 l sodium chloride solution (50 g NaCl/l) and the electrolyte solution was continuously circulated between the two vessels by a rotary pump. Two tantalum baskets, of which the sides were in the form of sieves and which were filled with Ni briquettes, were suspended in the electrolysis cell. The tantalum baskets were connected as anode and pure nickel plates connected as cathode were arranged opposite the sides so that the total electrode surface area was 0.5 m². Electrolysis was carried out with 4.2 V/500 A at a current density of 1000 A/m². During electrolysis, 200 ml per hour of a solution of nickel sulfate and cobalt sulfate (250 g $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ /l; 250 g/l $\text{CoSO}_4 \cdot 7 \text{H}_2\text{O}$) were continuously introduced into the electrolysis cell.

After 5 h, 40 l/h of the suspension formed was continuously removed from the circulation vessel and, at the same time, fresh sodium chloride solution was pumped into the electrolysis cell so that the liquid volume in the electrolysis reactor remained constant. The suspension was then filtered in batches and, in the further course of the electrolysis process, the filtrate was returned to the

electrolysis cell instead of the fresh sodium chloride solution. Accordingly, the additional sodium chloride solution was only used in the initial phase of the continuous process, after which a closed loop was established under steady-state reactor operating conditions. The suspension was easy to filter, giving a gel-like main product with a water content of on average 90%. The water removed was returned to the system as washing water for the gel-like main product. Chemical analysis revealed an average sulfate content of 1.8% and an average chloride content of 2% in the dried gel. The overall duration of the test was 105 h. In continuous operation, a total of 870 kg gel-form main product was obtained over that period.

b) Conditioning in NaOH

200 kg of the moist gel-like main product from the electrolysis reactor were finely dispersed by intensive stirring with 200 l water in a heated double-jacket reactor. The pH was then adjusted to 13.7 with NaOH, after which the suspension was heated with stirring to 80°C and kept at that temperature for 6 h.

The suspension was then filtered through a nutsch filter and the product from the nutsch filter was washed with water. After drying in a drying cabinet, 19.7 kg nickel hydroxide powder containing 1% Co were obtained. The anionic impurities of the dry powder amounted to less than 500 ppm. The apparent density (ASTM B-329) was 1.3 g/cm³ and the tamped density (ASTM; B-527) 1.8 g/cm³. The specific BET surface (as measured by the nitrogen method - ASTM D-1993) showed the very high value of 88 m²/g. The half-intensity width of the 101 reflex was 2.0.

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CLAIMS:

1. A process for the production of substantially pure nickel hydroxide, comprising the steps of:

(a) providing a metallic nickel source material in an aqueous electrolyte solution comprising sulfate ions and chloride ions, wherein the concentration of sulfate ions is in the range of 0.001 to 2.0 molar and the concentration of chloride ions is in the range of 0.3 to 5 molar, and wherein the molar ratio of chloride to sulfate ions is in the range of from 200:1 to 1:1;

(b) conducting a substantially continuous anodic oxidation of the nickel in the aqueous electrolyte solution to form nickel hydroxide, while maintaining said concentrations of sulfate and chloride ions and said molar ratio of chloride and sulfate ions, and maintaining a pH of 6 to 13 in the aqueous electrolyte solution, and removing formed nickel hydroxide from the aqueous electrolyte solution;

(c) treating the nickel hydroxide from step (b) by exposure, in a post-anodic treatment solution, to an alkali metal hydroxide at a concentration of 10^{-3} to 2 molar for a period of 1 to 48 hours at a temperature of 20 to 80°C and at an elevated pH compared to the pH of the aqueous electrolyte solution; and

(d) filtering and drying the product of step (c) to thereby obtain a substantially pure nickel hydroxide product with high density, high surface area and a high degree of crystallinity.

2. A process as in claim 1, wherein:

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(a') the concentration of sulfate ions in the aqueous electrolyte solution is 0.01 to 1.0 molar, the concentration of chloride ions in the aqueous electrolyte solution is 0.5 to 2 molar and the ratio of chloride to sulfate ions in the aqueous electrolyte solution is in the range of from 100:1 to 10:1, at least one of the chloride and sulfate ions is provided to the aqueous electrolyte solution as a salt thereof selected from the group consisting of nickel and alkali metal salts thereof, and further comprising the introduction of metal ions into the aqueous electrolyte solution from a source of metal selected from the group consisting of cadmium, cobalt, zinc and combinations thereof, and anodically freeing the metal ions from at least one said source of metal into the aqueous electrolyte solution during the anodic oxidation of the nickel;

(b') maintaining during the anodic oxidation said concentrations of sulfate and chloride ions, said molar ratio of chloride and sulfate ions and a pH of 8 to 12; and

(c') the alkali metal hydroxide of the post anodic treatment solution being provided in a range of 10^{-2} to 0.5 molar.

3. A process as in claim 1 or 2, wherein a pH value of 8 to 12 is maintained in the aqueous electrolyte solution.

25 4. A process as in claim 1, 2 or 3, wherein both the sulfate and chloride ions are provided to the aqueous electrolyte solution in the form of salts thereof selected from the group consisting of alkali metal and nickel salts.

5. A process as in any one of claims 1 to 4, effected in the presence of one or more additional metal values via

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metal salts selected from the group consisting of magnesium and calcium salts.

6. A process as in claim 5, wherein the metal salts are provided as salts with anions selected from the group
5 consisting of sulfate and chloride.

7. A process as in claim 1, further comprising the use of a secondary anode comprising a metal selected from the group consisting of cadmium, cobalt, magnesium, calcium, zinc and mixtures thereof during the anodic oxidation of the
10 nickel.

8. A process as in any one of claims 1 to 7, wherein the alkali metal hydroxide is potassium or sodium hydroxide.

9. Use of the substantially pure nickel hydroxide produced in accordance with the process of any one of claims
15 1 to 8, as an anode material in a nickel/cadmium or nickel hydride battery.

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PATENT AGENTS