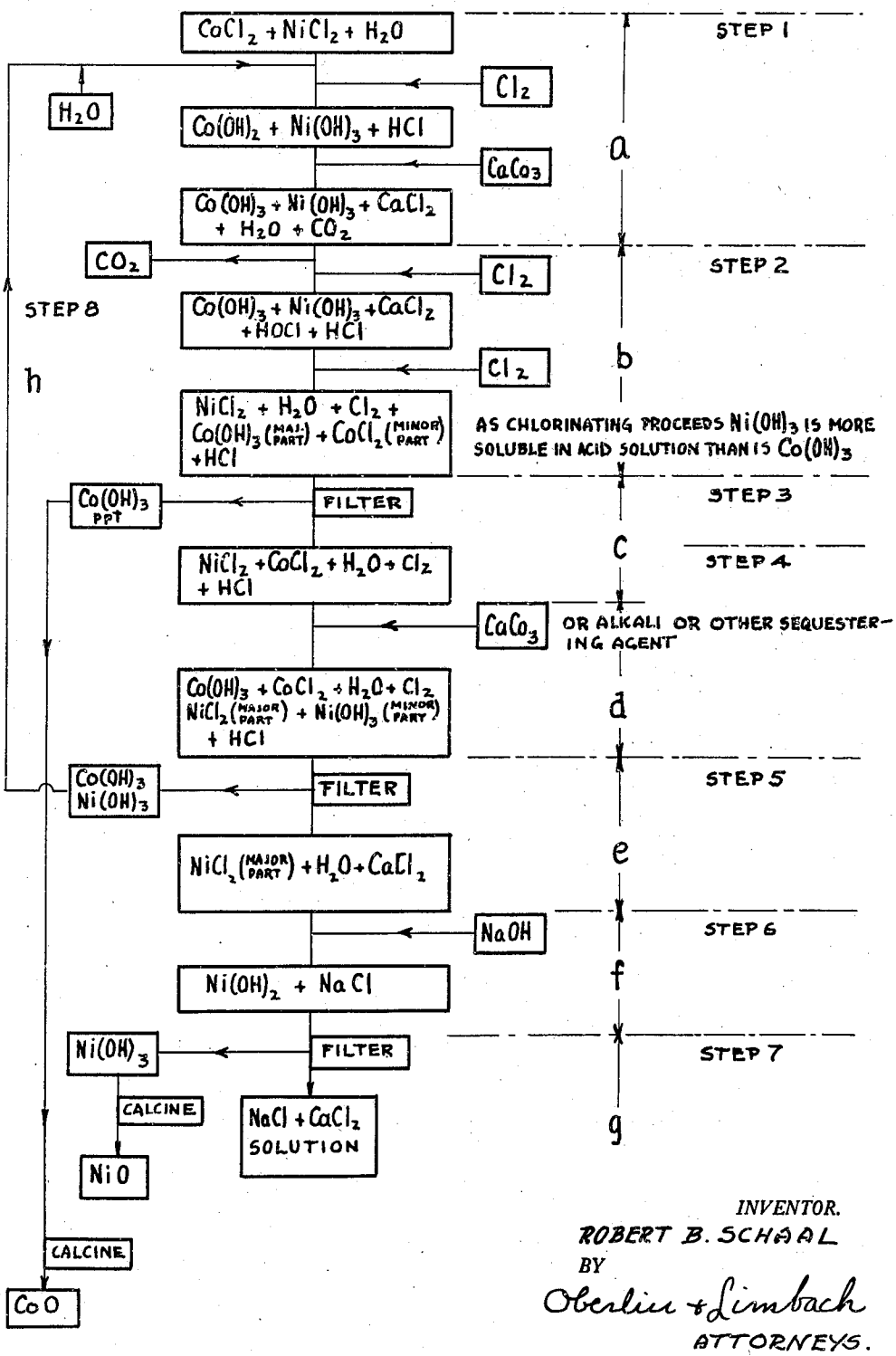
Nov. 22, 1949 R. B. SCHAAL 2,488,561

METHOD FOR THE SEPARATION OF COBALT AND NICKEL FROM SOLUTIONS

Filed Sept. 30, 1943



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Patented Nov. 22, 1949

2,488,561

UNITED STATES PATENT OFFICE

2,488,561

METHOD FOR THE SEPARATION OF COBALT AND NICKEL FROM SOLUTIONS

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Application September 30, 1943, Serial No. 504,382

6 Claims. (Cl. 23—183)

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This invention relates as indicated to the method for the separation of cobalt and nickel from solutions, and is especially useful as a further step in the general process of refining cobalt ores as disclosed in my copending application, Serial No. 371,509, filed December 24, 1940, now Patent No. 2,379,659.

The process of my said application concludes with a double chloride solution of cobalt and nickel. Such solution may also contain minor amounts of other chlorides with which, however, the present process is not concerned.

It is a principal object of the present invention to provide a process by which the cobalt and nickel components of a double chloride solution may be separated therefrom in substantially pure form with each component, i. e. nickel or cobalt, uncontaminated by any substantial amounts of the other component.

Other objects of my invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, said invention then comprises the features hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various ways in which the principle of the invention may be employed.

Broadly stated, this invention comprises the process which is characterized in that the cobalt and nickel components are first converted to the corresponding hydroxide. Substantially all of the nickel hydroxide is then reconverted along with only some of the cobalt hydroxide into the corresponding chlorides, permitting a recovery at this point of a substantial amount of the cobalt in the form of the hydroxide, and then reconverting the chlorides thus formed so as to precipitate substantially all of the cobalt as the hydroxide, and only some of the nickel as the hydroxide, leaving for further reconversion and recovery a substantial amount of the nickel free from any substantial amount of cobalt.

For a fuller understanding of my invention, the process may be explained by having detailed reference to the various steps performed.

In said annexed flow sheet

Step 1

The double chloride solution of nickel chloride and cobalt chloride available for example from the process of my said copending application is

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first treated by bubbling chlorine gas therethrough or in any other suitable fashion, in the presence of an alkali such as calcium carbonate resulting in the following representative reaction:

A. $2CoCl_2+Cl_2+6H_2O \rightarrow 2Co(OH)_3+6HCl$

The foregoing reaction is indicative of only the conversion of the cobalt chloride to the corresponding hydroxide. A similar equation might be written for the conversion of the nickel chloride to nickel hydroxide. Throughout the following description of this invention, however, representative formulas will only be given for the conversion of the cobalt component since duplication of such reactions for the nickel component is believed unnecessary to those skilled in the art.

This chlorination step is carried on with the presence in the solution of a sufficient amount of an alkali such as calcium carbonate so as to also combine with all of the HCl formed during the conversion of all of the chlorides in this first chlorinating step. The representative reaction by which the calcium carbonate thus removes or sequesters the HCl is as follows:

B. $6HCl+3CaCO_3 \rightarrow 3CaCl_2+3H_2O+3CO_2$

Step 2

After using up all the alkali by Step 1, Step 2 comprises chlorination in the absence of alkali.

The excess chlorine passed into the solution by this overchlorination step combines with water forming hypochloric acid and hydrochloric acid in accordance with the following representative reaction:

C. $Cl_2+H_2O \rightarrow HOCl+HCl$

The hydrochloric acid thus formed by reaction C above makes the solution progressively more acid as the chlorination step progresses. The cobalt hydroxide and nickel hydroxide present are soluble in such acid solution in accordance with the following representative equation:

D. $6HCl+2Co(OH)_3 \rightarrow 2CoCl_2+6H_2O+Cl_2$

The nickel hydroxide is more soluble than the cobalt hydroxide in the weakly acid solution formed during the early stages of overchlorination so that the nickel hydroxide is progressively dissolved at a more rapid rate than the cobalt hydroxide. It will generally be found, however, that while the nickel hydroxide is thus more soluble in the weaker acid solution, nevertheless,

by the time substantially all of the nickel hydroxide has thus been dissolved, a small portion of the cobalt hydroxide will also have been dissolved.

Step 3

The solution resulting from the overchlorination Step 2 above will contain substantially all of the nickel in the form of nickel chloride and only a minor proportion of the cobalt in the form of cobalt chloride. The major proportion of the cobalt will be left as precipitated cobalt hydroxide, which may be removed by filtration.

This step, therefore, is the one which yields the segregated cobalt in the form of the hydroxide which is substantially free from nickel and which may be converted to cobalt oxide by being dried and calcined.

Step 4

The filtrate resulting from Step 3 above is acid, and saturated with chlorine due to the overchlorination Step 2 above. In this fourth step, a sufficient amount of an alkali or other HCl sequestering reagent, such as calcium carbonate, is added to the filtrate in an amount sufficient to neutralize the excess acid, thus permitting the converting of substantially all of the cobalt chloride and only some of the nickel chloride into the corresponding hydroxides. Because the nickel chloride is more soluble in the weaker acid solution, the cobalt chloride will first be converted to the corresponding hydroxide as the HCl sequestering reagent removes the hydrochloric acid from the solution. Accordingly, by adding an excess amount of the HCl sequestering reagent, all of the cobalt chloride will be converted to cobalt hydroxide, and, depending upon the final acidity after the reaction ends a small but minor amount of the nickel chloride will be converted into the corresponding hydroxide, leaving a major proportion of the nickel chloride in solution.

Step 5

The product of Step 4 above is then filtered, removing from the solution substantially all of the cobalt in the form of the hydroxide, and only a minor amount of the nickel in the form of the hydroxide, leaving in the filtrate substantially no cobalt chloride but a substantial amount of nickel chloride.

Step 6

The filtrate resulting from Step 5 above, and containing a substantial amount of the nickel in the form of the chloride and substantially no cobalt, is then precipitated with sodium hydroxide, whereby the nickel chloride is converted to the hydroxide as follows:

E. $NiCl_2 + 2NaOH \rightarrow Ni(OH)_2 + 2NaCl$

Step 7

The suspension of nickel hydroxide resulting from Step 6 above is then filtered, separating the nickel hydroxide. This is the step which yields the segregated nickel in the form of the hydroxide substantially free from cobalt. The nickel hydroxide thus segregated may then be converted to the oxide by drying and calcining.

Step 8

It will be recalled that in Step 4 above, there was formed a mixture of cobalt and nickel hydroxides which were then removed by filtering in Step 5. This mixture of hydroxides in this Step 8 is then repulped with water and added to further cobalt-nickel chloride liquor used in Step 1 above, so that the amounts of cobalt and nickel included in this mixture of hydroxides will pass through the remaining sequence of steps and be ultimately recovered either as cobalt in Step 3, or as nickel in Step 7.

As an indication of relative quantities of the materials in the various steps as above outlined, in a commercial operation in accordance with the process of my invention, the following is submitted:

Analysis of combined chloride solution (mother liquor):

Co—2.05 g./l.
Ni—10.40 g./l.

Volume of chloride solution taken, 1000 gal. ⟷:

Co—17.1#
Ni—86.8#

Mixed cake from previous chlorination; weight taken wet 12.7#.

Analysis:

Co—13.1%
Ni—2.6%
H_2O—62%
$CaCO_3$—8%

Weights added in mixed cake:

Co—1.66#
Ni—.33#
$CaCO_3$—1.02#

Totals added as solution plus mixed cake:

Co—18.76#
Ni—87.13#
$CaCO_3$—1.02#

Calcium carbonate added in addition to above, 46.6#. Chlorine added, 35#, agitated 15 min.

On filtering and washing the following products were obtained:

(*a*) Liquid, 1205 gal., containing
Co—.18 gm./l.=1.8#
Ni—8.65 gm./l.=87.0#

(*b*) Filter cake, 88.7#, containing
Co—19.21%=17.04#
Ni—.16%=.14#
H_2O—63.0%

To the 1205 gal. liquid (*a*) was added 35# $CaCO_3$ (Step 4) and agitated until the liquid contained no further cobalt. It was then filtered and washed, obtaining:

(*c*) Liquid filtrate, 1378 gal., containing
Co—None
Ni—7.5 gm./l.=86.3#Ni

(*d*) Filter press cake, 16.6#, containing
Co—10.8%=1.8#
Ni—2.4%=.4#
$CaCO_3$—9.1%
H_2O—66.2%

Balance:

	Co	Ni
In Solution (*c*)	0.00#	86.30#
In Cake (*b*)	17.04#	.14#
In Cake (*d*)	1.80#	.40#
Total accounted for	18.84#	86.84#
Added	18.76#	87.13#

The cake (*a*) on drying, calcining, and pulverizing yielding 23.0# of black oxide powder, analyzing:

Co—70.85% ⟷ 16.29# Co
Ni—.58% ⟷ .13# Ni

The cake contained, in addition, small quantities of Fe, Cu, and Mn, with a trace of lead, as well as a little SiO_2 and Al_2O_3, these impurities being due to slightly imperfect prior separation and impurities introduced in the calcium carbonate.

The nickel solution (*c*) was precipitated by caustic soda, filtered, washed by several repulpings and intervening filtrations, dried, calcined, pulverized and weighed. It produced a silvery gray powder, weighing 109#, and analyzing:

Ni—75.1%=81.8# Ni

There were small quantities of Fe, Cu, CaO, CO_2, Cl_2 and alkalies in this cake with traces of Mn and Pb. The losses are due to the mechanical operations indicated.

I am aware of the fact that prior workers in the art have suggested that when chlorine is passed through a cold solution containing cobalt and nickel, and chlorides in the presence of calcium carbonate, cobaltic hydroxide precipitates leaving nickel chloride in solution. Strictly speaking, however, these prior art processes are useful only in the case of solutions so dilute as to be of no commercial application. Otherwise, some nickel co-precipitates with the cobalt.

The process which I have provided, however, insures sequential separation of the nickel and cobalt, without either being contaminated to any substantial extent by the other, irrespective of the relative concentrations of the two in the starting material.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims or the equivalent of such be employed.

I, therefore, particularly point out and distinctly claim as my invention:

1. The method of separating cobalt from a double chloride solution of cobalt and nickel which comprises: (*a*) chlorinating the solution, in the presence of a stoichiometric amount of calcium carbonate required to react with the hydrochloric acid produced, sufficently to precipitate substantially all of the chlorides of cobalt and nickel present in the solution as the corresponding hydroxides, (*b*) further chlorinating to an extent sufficient to redissolve substantially all of the nickel hydroxide and only a minor amount of the cobalt hydroxide as the corresponding chlorides and with the production of free hydrochloric acid, and then (*c*) separating the remaining cobalt hydroxide from the solution.

2. The method of separating cobalt and nickel from a double chloride solution thereof which comprises: (*a*) chlorinating the solution, in the presence of a stoichiometric amount of calcium carbonate required to react with the hydrochloric acid produced, sufficiently to precipitate substantially all of the chlorides of cobalt and nickel present in the solution as the corresponding hydroxides, (*b*) further chlorinating to an extent sufficient to redissolve substantially all of the nickel hydroxide and only a minor amount of the cobalt hydroxide as the corresponding chlorides and with the production of free hydrochloric acid, (*c*) separating the remaining cobalt hydroxide from the solution, and then (*d*) recovering the nickel from the filtrate.

3. The method of separating cobalt and nickel from a double chloride solution thereof which comprises: (*a*) chlorinating the solution, in the presence of a stoichiometric amount of calcium

carbonate required to react with the hydrochloric acid produced, sufficiently to precipitate substantially all of the chlorides of cobalt and nickel present in the solution as the corresponding hydroxides, (*b*) further chlorinating to an extent sufficient to redissolve substantially all of the nickel hydroxide and only a minor amount of the cobalt hydroxide as the corresponding chlorides and with the production of free hydrochloric acid, (*c*) filtering the remaining cobalt hydroxide from the solution, (*d*) converting substantially all of the cobalt chloride and some of the nickel chloride in the filtrate into the corresponding hydroxides by adding calcium carbonate, (*e*) filtering from the solution the cobalt hydroxide and nickel hydroxide so formed, and then (*f*) recovering the nickel from the filtrate.

4. The method of separating cobalt and nickel from a double chloride solution thereof which comprises: (*a*) chlorinating the solution, in the presence of a stoichiometric amount of calcium carbonate required to react with the hydrochloric acid produced, sufficiently to precipitate substantially all of the chlorides of cobalt and nickel present in the solution as the corresponding hydroxides, (*b*) further chlorinating to an extent sufficient to redissolve substantially all of the nickel hydroxide and only a minor amount of the cobalt hydroxide as the corresponding chlorides and with the production of free hydrochloric acid, (*c*) filtering the remaining cobalt hydroxide from the solution, (*d*) converting substantially all of the cobalt chloride and some of the nickel chloride in the filtrate into the corresponding hydroxides by adding calcium carbonate, (*e*) filtering from the hydroxide so formed, leaving in the filtrate substantially no cobalt chloride but a substantial amount of nickel chloride, (*f*) converting substantially all of the nickel chloride into the corresponding hydroxide by adding sodium hydroxide, and then (*g*) filtering the nickel hydroxide from the product of step (*f*).

5. The method of separating cobalt and nickel from a double chloride solution thereof which comprises: (*a*) chlorinating the solution, in the presence of a stoichiometric amount of calcium carbonate required to react with the hydrochloric acid produced, sufficiently to precipitate substantially all of the chlorides of cobalt and nickel present in the solution as the corresponding hydroxides, (*b*) further chlorinating to an extent sufficient to redissolve substantially all of the nickel hydroxide and only a minor amount of the cobalt hydroxide as the corresponding chlorides and with the production of free hydrochloric acid, (*c*) filtering the cobalt hydroxide precipitate from the solution, (*d*) adding to the filtrate an amount of calcium carbonate sufficient to neutralize the free hydrochloric acid from the previous step and substantially all of the cobalt chloride and only a small but minor amount of the nickel chloride are converted into the corresponding hydroxides, (*e*) filtering from the hydroxide so formed, leaving in the filtrate substantially no cobalt chloride but a substantial amount of nickel chloride, (*f*) converting substantially all of the nickel chloride in the filtrate into nickel hydroxide by adding sodium hydroxide, (*g*) filtering the nickel hydroxide from the product of step (*f*), and then (*h*) repulping the hydroxide mixture removed by step (*e*) for addition to further liquor used in step (*a*).

6. The method of separating cobalt and nickel from a double chloride solution thereof which

comprises: (*a*) chlorinating the solution, in the presence of a stoichiometric amount of calcium carbonate required to react with the hydrochloric acid produced, sufficiently to precipitate substantially all of the chlorides of cobalt and nickel present in the solution as the corresponding hydroxides, (*b*) in the absence of calcium further chlorinating to an extent sufficient to redissolve substantially all of the nickel hydroxide and only a minor amount of the cobalt hydroxide into the corresponding chloride with the production of free hydrochloric acid, and then (*c*) filtering the remaining cobalt hydroxide from the solution, (*d*) adding to the filtrate an amount of calcium carbonate sufficient to neutralize excess hydrochloric acid substantially all of the cobalt chloride and only some of the nickel chloride being converted into corresponding hydroxides, (*e*) filtering from the hydroxide so formed, leaving in the filtrate substantially no cobalt chloride but a substantial amount of nickel chloride, (*f*) converting substantially all of the nickel chloride in the filtrate into nickel hydroxide by adding sodium hydroxide, (*g*) filtering the nickel hydroxide from the product of step (*f*), and then (*h*) repulping the hydroxide mixture removed by step (*e*) for addition to further liquid used in step (*a*).

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