UNITED STATES PATENT OFFICE.

MARVIN J. UDY, OF KOKOMO, INDIANA, ASSIGNOR TO HAYNES STELLITE COMPANY, OF KOKOMO, INDIANA, A CORPORATION OF INDIANA.

PROCESS OF RECOVERING COBALT.

1,336,765. Specification of Letters Patent. Patented Apr. 13, 1920.

No Drawing. Application filed August 14, 1919. Serial No. 317,457.

To all whom it may concern:

Be it known that I, MARVIN J. UDY, a citizen of the United States, residing at Kokomo, in the county of Howard and State of Indiana, have invented certain new and useful Improvements in Processes of Recovering Cobalt, of which the following is a specification.

This invention relates to processes of recovering cobalt; and it comprises a method of producing cobalt (or nickel) from an ore containing the same wherein such ore is submitted to an oxidizing roast to produce soluble sulfates, such sulfates brought into solution and submitted to various purificatory treatments, the purified sulfates converted into basic form and the basic material used to replenish a metal-depositing slightly acid electrolytic bath operating with an insoluble anode; all as more fully hereinafter set forth and as claimed.

It is the object of the present invention to provide a simple, cheap and ready method of recovering cobalt (or nickel) in the metallic state from its ores with the aid of the electrolytic current. As I have found, if a bath of cobalt sulfate solution be kept slightly acid and electrolyzed with an insoluble anode, the metal may be readily and efficiently thrown down by the current. The current efficiency of electrolysis is between 80 and 95 per cent. with an acidity ranging between 0.3 and 1 per cent. free sulfuric acid. Good electrolysis may be obtained with larger per cents. of acid but the efficiency steadily decreases with increased acidity until with 8 per cent. acid there is only about 5 per cent. current efficiency. With an acidity maintained not higher than about 1 per cent., the voltage required is about 0.5 to 2 volts less than in a strictly neutral solution while the current efficiency is as great. In a neutral solution cobalt tends to deposit on the anode more or less as one of the higher oxids; this tendency being particularly great with bright, clean anodes. With a slightly acid electrolyte there is less of this tendency. In operating with an insoluble anode and controlled acidity, the excess of acid developed in electrolysis must be neutralized from time to time or continuously.

Similar facts obtain with a solution of nickel sulfate; or with a solution containing both cobalt and nickel sulfates.

In the present invention I take advantage of the noted facts in providing a method of extracting cobalt (or nickel) from its ores. Cobalt (and nickel) ores are of varied nature and may contain many constituents; but in all cases the cobalt (and nickel) go over into comparatively stable, water-soluble sulfates when the ore is roasted in the presence of sufficient sulfur or sulfuric acid. Various other constituents also go into water-soluble form but these can be removed from the solution by the various operations hereinafter set forth. From the purified solutions, basic sulfates can be precipitated by a regulated addition of alkali and these then used in maintaining an electrolytic bath.

I first roast the ore at a controlled temperature with free access of air. Many of the common cobalt ores contain arsenic which on roasting tends to go over to cobalt arsenate which is soluble in acids. Copper if present also tends to become arsenate. In the absence of arsenic, cobalt tends to form higher oxids which are not readily soluble in acids in the absence of reducing agents. In the present operation therefore I ordinarily add sulfuric acid prior to roasting. Sometimes, but not often, a second addition of acid and a second roast are necessary. Sulfur, pyrites, etc., may be used in lieu of sulfuric acid; but it is better to use the acid. Where the ore contains sulfur in sufficient amounts, it is not necessary to add more. As a result of the sulfating or acid roast nickel and cobalt are converted into sulfates as is the copper while some or much of the iron also becomes soluble as sulfate; the proportion of soluble iron sulfate depending somewhat on the roasting conditions. More or less of the arsenic is also converted into a form soluble in the leachings from the acid roast. In the event that sulfuric acid is used, and sometimes without its use, the roast may ball up or clinker to an extent requiring a subsequent crushing or grinding. The roasted material, if the operation is carefully effected, should contain all the cobalt in the form of a soluble sulfate. The soluble sulfates are dissolved by adding water to the roasted material, with or without grinding as the case may be. In dissolving the sulfates in water, either mechanical or air agitation is usually desirable. Heating may be necessary. The magma of ore and liquid is usually sent through an ordinary filter press

or the like for separation of the solution from the insoluble residue, and the latter is washed with water. Very often, the residue left on filtration and washing is so barren of cobalt or other values that it may be discarded. If not, it is retreated.

The solution so obtained is treated with calcium carbonate, which may be any of the commercial forms or may be air-slaked lime, and is air-blown. This treatment is effected at room or atmospheric temperature. Under the influence of this treatment with air and calcium carbonate, nearly all the bases other than cobalt and nickel are precipitated. Under the influence of the air and base, the ferrous salts oxidize to ferric and give a precipitate which carries down arsenic. Copper arsenate and calcium arsenate may also be thrown down in the order stated. In the absence of sufficient arsenic, copper remains in solution and may have to be removed in the next step. If there is not enough iron in the solution to take care of arsenic, etc., some may be added in the form of sulfate of iron. After treatment of the liquid with calcium carbonate and air, the material is filter-pressed and the press cake washed. It may be treated to recover contained values or discarded, as the case may be. The solution is neutral and contains the cobalt. Nickel is also in solution if present.

If this solution is treated with enough soluble alkali, such as milk of lime, all the cobalt and nickel are thrown down as protoxids, that is as cobaltous and nickelous oxids, respectively. If lime sufficient for complete reaction or to make the mixture alkaline be used, the precipitation must be so conducted as to obviate access of air to the precipitate as much as possible; since cobalt oxid has the inconvenient property of oxidizing on exposure to air (especially if there is much alkali retained), which renders the material not so suitable for my subsequent purposes. Therefore, I customarily add lime in amount not quite sufficient to throw down all the cobalt and nickel, leaving a little still in the solution. The solution may be returned for reuse in leaching in order to regain this residual cobalt or nickel. In so operating the character of the precipitate so obtained varies with the ore and the circumstances, but in a general way it may be said to consist of calcium sulfate, basic sulfates of cobalt and of nickel, and often, more or less hydroxids. If copper is still present it occurs in the precipitate.

The cobalt sulfates in the precipitate so produced, unlike the oxids do not further oxidize on exposure to the air and become insoluble in acids but retain their reactivity toward acids indefinitely. The basic cobalt sulfates are taken up to form neutral sulfate solutions by even very weak solutions of sulfuric acid, leaving the admixed calcium sulfate behind. It is therefore admirably adapted for use in keeping an electrolytic sulfate bath of adjusted acidity and it is here so used.

A suitable solution of cobalt sulfate in a suitable electrolytic cell having an insoluble anode is submitted to electrolysis to regain the metal. Lead anodes and aluminum cathodes may be employed and the deposited cobalt stripped from the cathode from time to time. It is very pure. The same operation takes place where the solution is one of nickel sulfate. As the electrolysis goes on, there being an insoluble anode, the bath becomes acid in proportion to the amount of deposit. Unless this acidity be restrained, the efficiency, for the reasons previously stated, steadily decreases. I therefore aim to maintain this developed acidity between 0.3 and 1 per cent. free sulfuric acid, neutralizing any excess of acid over these limits with the aid of the basic sulfate. Neutralization may be effected by placing in the bath the proper amount of precipitated basic sulfate made as hereinbefore described, but since this also introduces calcium sulfate as a mud, I find it better to remove portions of the bath from time to time or continuously and neutralize in an outside vessel of some type. In so doing, the basic sulfate is taken up, neutralizing the free acid, and the calcium sulfate remains undissolved. It may be separated from the neutralized bath liquor by decantation or filtration. For example, the removed bath liquor may be allowed to flow into a neutralizing vat containing precipitated basic sulfate and then through a filter, back to the cell.

Any accumulation of sulfuric acid in the system is gotten rid of by adding some calcium carbonate with the basic sulfates, precipitating it as calcium sulfate which is removed together with that added with the basic sulfates. In the event the solution contains copper, it may be removed by electrolyzing it in a special cell using a low voltage; or by treating the liquid with metallic cobalt (or nickel).

In the event that both nickel and cobalt occur in the ore and that it is desirable to separate them this may be done in any of the usual ways. If they are not separated they come out together as metals in the present method.

What I claim is:—

1. The process of recovering metals of the cobalt class from their ores which comprises submitting such an ore to a sulfating roast, extracting the soluble sulfates with water, precipitating the sulfate solution with calcium carbonate in the presence of air and finally precipitating with alkali added to a point short of neutralizing acidity.

2. The process of recovering metals of the

cobalt class from their ores which comprises submitting such an ore to a sulfating roast, extracting with water, precipitating with calcium carbonate in the presence of air, finally precipitating with alkali added to a point short of neutralizing acidity, establishing and maintaining electrolysis of a slightly acid sulfate bath with the aid of an insoluble anode, and treating such a bath with the alkali-precipitated material in the amount sufficient to maintain the acidity below one per cent. of sulfuric acid.

3. The process of recovering metals of the cobalt class from their ores which comprises submitting such an ore to a sulfating roast in the presence of sulfuric acid, extracting soluble sulfates with water, precipitating with calcium carbonate in the presence of air, removing copper by contacting the solution with metal of the kind to be recovered, precipitating with lime in amount merely sufficient to form a basic insoluble sulfate, electrolyzing a sulfate bath with an insoluble anode and dissolving portions of said basic sulfate therein in proportion to the observed tendency for the acidity of said bath to rise above a normal point.

4. In the manufacture of metals of the cobalt class, the process which comprises electrolyzing a solution of a sulfate of such a metal with an insoluble anode and neutralizing said solution in proportion to the developed acidity by means of a basic sulfate of such metal.

5. In the manufacture of metals of the cobalt class, the process which comprises electrolyzing a slightly acid solution of a sulfate of such a metal with an insoluble anode, the acidity being maintained at a point not exceeding one per cent. free H_2SO_4 by additions of a basic compound of such metal.

In testimony whereof, I affix my signature hereto.

MARVIN J. UDY.