This invention relates to the electrolytic refining of nickel, particularly the purification of nickel electrolytes, and has for its objects certain improvements in the method of purifying nickel electrolytes employed in the electrolytic refining of nickel.

In the electrolytic refining of nickel, that is in the production of primary nickel in the form of nickel cathodes, as now practiced in the Hynineet process, for example, an objectionable amount of iron tends to follow the nickel through the smelting and into the electrolytic operation. Impure nickel is used as anodes. The anodes go into solution during the electrolysis step, and most of their impurities, such as iron, lead, arsenic and copper, find their way into the electrolyte, usually consisting of an aqeous solution of nickel sulfate. The electrolyte thus contaminated is subjected to a purification operation before it is used for the electrolytic deposition of nickel. While substantially all of the impurities may be removed from the electrolyte by processes heretofore employed, sufficient traces of some of the impurities remain which for special purposes at least may perceptibly impair the quality of the resulting cathodes and the products made from them. Therefore, a demand for nickel of even greater purity.

To keep the iron out of the cathodes, it is necessary to remove it from the electrolyte. A common method is to blow air into the electrolyte to oxidize the iron and precipitate it as ferric hydroxide. The formation of the ferric hydroxide results in the release of acid. As the acidity of the electrolyte increases, a point is reached at which the ferric hydroxide begins to dissolve in the electrolyte, or at which no more ferric hydroxide is formed. To avoid dissolution of the ferric hydroxide and to permit the formation of further amounts of ferric hydroxide, it is customary to add a neutralizing agent, such as nickel carbonate, to the electrolyte to neutralize the released acid.

The introduction of neutralizing substances, such as nickel carbonate, in the electrolyte is expensive. An excess must be employed. The lower the temperature of the electrolyte, the longer it takes to neutralize the excess acid. Some of the excess nickel carbonate necessarily becomes admixed and is removed with the ferric hydroxide.

The practice becomes complicated if there is no ready source of nickel, such as nickel sulfate, other than the nickel electrolyte, with which to make the nickel carbonate. If the nickel electrolyte is the source of the nickel for making the nickel carbonate, the nickel content of the electrolyte may be depleted to such an extent as seriously to impair the quality of the nickel deposited on the cathodes. The use of neutralizing substances also necessarily introduces foreign soluble salts in the electrolyte, which in due course may cause trouble because of a too high concentration of such salts.

As a result of our investigations, we have discovered that these disadvantages may be substantially overcome. The impure electrolyte coming from the electrolytic cells is made to contain only a limited amount of iron so that when it is aerated, substantially all of the objectionable iron is oxidized and converted to ferric hydroxide before enough acid is released to require the neutralizing step heretofore employed. In other words, the electrolyte before it is aerated contains substantially no more iron in solution than can be precipitated solely by aeration. This eliminates the necessity of adding neutralizing substances to the electrolyte and the electrolyte is therefore not impaired by the presence of too much foreign soluble salts.

As is well known in the art, the ferric hydroxide resulting from the aeration step also functions as a scavenging agent because such additional impurities in the electrolyte as lead, arsenic and copper are adsorbed on the ferric hydroxide precipitate and are separated from the electrolyte simultaneously with the removal of the ferric hydroxide, usually by filtering. Nickel electrolyte purified in this manner, however, still contains residual amounts of lead, arsenic and copper. The object of the present invention is to remove a substantial amount of these residual impurities. This is done by subjecting the purified electrolyte to the additional purifying action of added ferric hydroxide especially prepared outside of the electrolyte by wet precipitation, the ferric hydroxide being introduced while still wet from the precipitation into the electrolyte in amount sufficient to adsorb thereon a substantial amount of the residual impurities. The acidity of the electrolyte as it comes from the previous purifying step with air
is insufficient to dissolve the added ferric hydroxide. The added ferric hydroxide and its adsorbed residual impurities are then separated from the electrolyte and the electrolyte thus purified is subjected to electrolysis to produce substantially pure nickel cathodes.

Impure nickel anodes are dissolved in the electrolyte as the substantially pure nickel cathodes are produced, and the resulting impure electrolyte containing the limited amount of iron is subjected to the steps set forth. While ferric hydroxide is introduced into the electrolyte, it is in a form that will not affect the electrolyte because the pH of the electrolyte is such that the added ferric hydroxide will not go into solution. The added ferric hydroxide precipitate is therefore made to function essentially as an inert solid scavenging agent in removing a substantial amount of the remaining residual metal impurities, lead, arsine and copper, in the electrolyte which are adsorbed on the added ferric hydroxide precipitate and are separated from the electrolyte with the ferric hydroxide precipitate.

As pointed out, the electrolyte coming from the electrolytic cell or anode mill is made to contain a limited amount of iron in solution so that when the electrolyte is subjected to aeration practically all of the iron is converted to ferric hydroxide which is separated from the electrolyte as a precipitate. In other words, the electrolyte is made to contain no more iron in solution than can be removed solely by the aeration step, thus eliminating the necessity of using neutralizing substances, such as nickel carbonate, to neutralize the excess acid formed by the hydrolysis of the iron during the aeration step. This highly desired result is made possible by using nickel anodes in the electrolysis, which in turn contain a limited amount of iron, so that when the anodes go into solution, an excess of iron is not released in the electrolyte; that is, substantially no more than can be precipitated solely by aeration.

To this end special precautions are followed in making the nickel anodes. In the production of the nickel anodes, nickel-copper matte is crushed, roasted, leached and subjected to a smelting operation. The principal metals, nickel, copper and iron, are present in the matte both in metallic and sulfide form. The crushed matte is roasted in the presence of air to oxidize most of the sulfur, thus converting the metallic and sulfide forms of nickel, copper and iron into the oxides of these metals. A small amount of sulfides, however, remains. The roasted material is leached usually with dilute sulfuric acid to extract the bulk of the copper as copper sulfate. Operating conditions are such that the leaching operation generally leaves about 12% copper in the residues or leached matte. The leached matte may be smelted in any suitable furnace.

In the present practice of the invention, to give an illustrative example, the leached matte is subjected to smelting in an electric furnace. Carbon, for instance in the form of anthracite fines, is used as the reducing agent, a small amount of flux, such as sand and lime being admixed with the carbon and leached matte. The carbon tends to exert a selective reduction reaction, in the following order: copper nickel (arsenide) and iron. Enough carbon is, therefore, employed not only to reduce the copper and nickel but also a substantial amount of the iron. Some of the iron passes into the slag, so that the removal of the slag results in the removal of some of the iron. The molten anode metal, containing the nickel and the remaining copper as well as small amounts of iron and other metal impurities, is then cast into impure nickel anodes.

A number of the impure nickel anodes are employed in each electrolytic cell during the electrolysis operation so that they gradually go into solution in the electrolyte as the desired nickel is deposited as nickel cathode. The anode contains preferably no more than about 0.3 to 0.4% iron, which is the amount that can be readily removed solely by aeration.

In the smelting of the leached matte an attempt is, therefore, made to obtain anode nickel containing not more than about 0.3 to 0.4% iron. It sometimes happens, however, that some of the nickel anodes contain a slight excess of iron, for example, 0.6% iron. On the other hand, in some other instances, the smelting operation results in nickel anodes containing substantially less iron, for example, 0.2% iron. While the exclusive use of anodes with the higher iron content would be objectionable, electrolyte of optimum iron content is obtained by employing such a mixture of the higher as well as the lower iron content. In other words, a nickel anode with 0.6% iron is used simultaneously with a nickel anode having 0.2% iron. In this manner the average iron content of the nickel anodes is kept below about 0.5%. Nickel anodes are selected whose combined iron content is substantially no more than can be thrown down solely by aeration when the anodes are dissolved in the electrolyte. In other words, the production of the nickel anode metal is so conducted that there will not be more than a predetermined amount of iron present. That predetermined amount of iron is fixed by the amount of iron that can be removed solely by aeration of the electrolyte coming from the electrolytic cell.

In a presently preferred practice of the invention, freshly prepared, wet and undried ferric hydroxide is added to the nickel electrolyte. They are left in intimate contact with one another until adsorption equilibrium is attained, so that the maximum amount of impurities are adsorbed by the ferric hydroxide. The ferric hydroxide may be added at any stage or stages in the treatment of the electrolyte.

The ferric hydroxide is advantageously added to nickel electrolyte that has already been treated according to a conventional purification operation to remove substantially all of the impurities under consideration. In other words, nickel electrolyte containing only minute amounts of the objectionable impurities is subjected to the ferric hydroxide treatment to remove a substantial amount of the remainder of the impurities. The preliminary purification operation may, for example, follow that disclosed in United States Patent 1,986,967 of January 8, 1935, to Gronningsaeter, according to which the electrolyte is subjected to the neutralizing and copper cementing action of finely divided highly reactive metallic nickel, preferably obtained by gas-reduction at a temperature only slightly above that required to effect reduction. The nickel is sufficient in amount and reactivity to cement the copper and most of the arsenic present, and to effect substantial neutralization of the electrolyte without the addition of any other neutralizing agent. That is, the electrolyte becomes only slightly acid. The mixture is then subjected to filtration to separate the resulting solid substances from the filtrate. The sludge or
The partially neutralized electrolyte filtrate is then subjected to aeration, or other suitable treatment, to effect precipitation of substantially all of the objectionable iron by oxidation and hydrolysis, which carries with it a substantial amount of such impurities as lead, arsenic and copper; after which the electrolyte is again filtered. The electrolyte before it is aerated contains substantially no more iron in solution than can be precipitated solely by the aeration; and the acidity of the electrolyte is insufficient to dissolve the ferric hydroxide so formed. The resulting filter cake is advantageously treated with acid to extract the nickel content of some; this solution is returned to the nickel electrolyte at some suitable point.

Freshly prepared ferric hydroxide, or at least ferric hydroxide still wet from its precipitation, is then added to the electrolyte thus purified, and the two are kept in intimate contact with one another until adsorption equilibrium is attained, whereby a substantial proportion of the remaining undesired impurities, such as lead, arsenic and copper, are adsorbed on the ferric hydroxide. At this point the electrolyte must be sufficiently non-acid or neutral so that the ferric hydroxide is not dissolved.

The electrolyte is then subjected to filtration, or other suitable separation treatment, to remove the precipitate with its adhering impurities; after which the filtrate is subjected to electrolysis to produce nickel cathodes in the conventional manner.

The accompanying flow-sheet illustrates a useful practice of the invention, and shows particularly how the various stages of the process may be inter-related to advantage. Inspection of the flow-sheet, in conjunction with the following description, will show, for example, certain cyclic features of the process that have considerable practical utility.

It is advantageous to conduct the purification treatment with ferric hydroxide in several stages. As noted above, it is conventional practice to subject the nickel electrolyte to (1) aeration to remove copper and to neutralize the electrolyte, most of the arsenic also being taken out at the same time, (2) aeration, or other treatment, to precipitate iron, and (3) filtration to remove the iron, after which the purified filtrate goes to the electrolytic cells. In our present practice of the invention, the former iron precipitation treatment is divided into two steps, as will be clear from the following description:

Referring to the flow sheet, it will be noted that the impure nickel electrolyte coming from the nickel deposition tanks (electrolytic cells), formed by the dissolution of impure anodes, is conducted to cementation tanks where it is subjected to the copper cementing and neutralizing action of highly reactive, finely divided gas reduced nickel powder, as noted above. The mixture is passed to a filter press where it is filtered.

The resulting filter cake of cement copper is conducted to a roaster, and is suitably treated to recover the copper. The filtrate of nickel electrolyte is passed to iron precipitation tanks, where it is subjected to aeration. As a result of this oxidizing treatment with air, nearly all of the iron present in the electrolyte is precipitated by hydrolysis to form ferric hydroxide, and some of the additional impurities, such as lead, arsenic and copper, are adsorbed thereon. The hydrolyzation of the trivalent iron is accompanied by liberation of acid, which means a decrease in pH.

The resulting mixture is again passed through a filter press. The filter cake containing the iron and adsorbed impurities is sent to nickel extraction tanks where it is subjected to the action of sulphuric acid or acidified nickel electrolyte to extract practically all of the available nickel as nickel sulphate, while the ferric hydroxide containing the adsorbed impurities is left undissolved. This mixture is filtered. The filter cake of ferric hydroxide and adsorbed impurities is discarded; while the nickel sulphate solution thus recovered is added to impure nickel electrolyte to be added to the nickel deposition tanks to the cementation tanks.

The filtered electrolyte thus obtained is passed to adsorption tanks where it is for a second time subjected to aeration. The repeated treatment with air is effective to oxidize and precipitate some of the remaining iron dissolved in the electrolyte. Freshly prepared ferric hydroxide is added to the solution at this stage. The two, including the ferric hydroxide formed in situ, are maintained in intimate contact, say for about two hours, until a substantial amount of the remaining impurities, such as lead, arsenic, and copper, are adsorbed on the two forms of ferric hydroxide.

This mixture is then passed to a filter press, and filtered. The filter cake is conducted to a re-cutting or re-bubbling tank, where it is suspended in nickel electrolyte comprising a part of the filtrate nickel electrolyte obtained from the filtering operation directly following the cementation step. The resulting suspension of nickel electrolyte and partly spent ferric hydroxide is conducted to the iron precipitation tank, and added to the other part of the filtrate nickel electrolyte obtained from the filtering operation directly after the cementation step. In this manner, the sludge of freshly prepared ferric hydroxide again functions with that formed in situ during the first aeration step to act as an adsorbent.

The electrolyte is, therefore, given a preliminary impurity adsorption treatment with specially added ferric hydroxide at the same time as iron contained in the electrolyte is first precipitated by aeration. A larger amount of the impurities is thus carried down than would be the case with aeration alone. The electrolyte is then filtered to remove the precipitate of iron containing the adsorbed impurities; and the filter cake is subjected to nickel extraction with acid or acidified nickel electrolyte, as mentioned above.

The filter cake is moved on to the adsorption tanks where it is again subjected to the action of air and freshly prepared ferric hydroxide, as noted above. The resulting mixture is filtered, the filter cake being reground as indicated above.

The nickel electrolyte is thus subjected to the adsorption action of ferric hydroxide in at least two stages of its treatment before it is subjected to electrolysis in the electrolytic cells. The last purification step with freshly prepared ferric hydroxide is performed at the normal pH value of the electrolyte and it does not cause any appreciable change in the pH value of the electrolyte. The operation may be conducted at the normal temperature of the electrolyte.

The resulting purified nickel electrolyte is passed into the nickel deposition tanks, provided with Hybinette bags, where it is subjected to electrolysis in the conventional manner to pro-
duce nickel cathodes. The cathodes contain only traces of such impurities as lead, arsenic and copper.

It will be clear from the foregoing description and the flow sheet that the invention lends itself to the practice of a number of important cyclic steps. The nickel deposition tanks are fed with a continuous flow of highly purified electrolyte, because the several cyclic steps assure a fairly complete removal of the impurities in question.

Investigation indicates that the freshly prepared ferric hydroxide has a greater affinity for the lead impurity, particularly, than the ferric hydroxide formed in situ during aeration of the electrolyte. This appears to be due to the difference in the amount of nickel hydroxide occluded by the respective ferric hydroxides. The ferric hydroxide formed in situ carries down a greater amount of nickel hydroxide than the freshly prepared ferric hydroxide specially added to the electrolyte; and the occluded nickel hydroxide appears to impair the adsorbent power of the ferric hydroxide for lead, perhaps in some proportion to the amount of nickel hydroxide occluded. Even if ferric hydroxide precipitated in situ is less reactive than pure ferric hydroxide prepared outside the electrolyte, it would of course be possible to obtain a better purification simply by introducing more iron in the solution. But when working according to the method just described, the amount of iron which can be precipitated is strictly limited owing to the drop in pH, and introduction of neutralizing substances are either expensive or may introduce foreign soluble salts into the electrolyte, which in due course may cause trouble because of a too high concentration of such salts.

The degree of purity obtainable in the practice of the invention will, of course, be dependent on the quantity of ferric hydroxide added, and the manner in which the nickel electrolyte is treated with the same. Generally speaking, the larger the amount of ferric hydroxide employed the more completely the impurities in question are removed, but, on the other hand, there are economic limits to the amount that should be employed. This limit will have to be determined for each case, and no fixed rule can be given. In any given case, optimum operating limits may be determined readily by a few trial and error tests.

In the present preferred practice of the invention, ferric hydroxide equivalent to about 40 grams of iron per cubic meter of nickel electrolyte is employed.

In order to show what can be accomplished in the practice of the invention, nickel cathodes were electrodeposited under exactly the same conditions, except that in the first case the electrolyte was subjected to a treatment with freshly prepared and specially added ferric hydroxide corresponding to 40 grams of iron per cubic meter of electrolyte, and in the other case the electrolyte was not treated with the freshly prepared and specially added ferric hydroxide but was of course treated with the ferric hydroxide formed in situ during the aeration step. To make the nickel cathodes nickel sulphate electrolyte containing about 50 grams of nickel per liter, 20–25 grams of sodium sulfate per liter and 25 grams of boric acid per liter was employed, the electrolyte having a pH of 5.5 directly as it came from the cementation and neutralization operation. 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 ampere per square decimeter. Analysis of the two nickel cathodes shows the following results:

<table>
<thead>
<tr>
<th>Treatment</th>
<th>NiO&lt;sub&gt;2&lt;/sub&gt;OP&lt;sub&gt;4&lt;/sub&gt;</th>
<th>FeO&lt;sub&gt;2&lt;/sub&gt;OP&lt;sub&gt;4&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treated</td>
<td>0.010</td>
<td>0.020</td>
</tr>
<tr>
<td>Not treated</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

The results show that the ferric hydroxide added was effective not only in removing arsenic and lead but also in removing some copper. The figures also show that a very substantial amount of the arsenic and lead were removed.

Beside metallic impurities, ferric hydroxide also adsorbs some organic impurities, and thus can also be utilized when the electrolyte is contaminated with too much of such substances. Nickel electrolytes of the character herein contemplated are frequently contaminated with traces of objectionable organic impurities, which are advantageously removed in the practice of the present invention.

The ferric hydroxide employed in the practice of the invention may be prepared in any suitable way, to give a sufficiently pure and reactive product. The ferric hydroxide may, for example, be prepared by dissolving scrap iron in dilute sulfuric acid, oxidizing the iron in concentrated solution to the ferric state by means of nitric acid, diluting the resulting ferric sulfate solution, and precipitating the iron as ferric hydroxide by means of caustic soda or ammonium. If larger amounts of sodium or ammonium sulfate are objectionable, the greater part of same can be removed by washing the resulting ferric hydroxide sludge with water until it is ready for use. The ferric hydroxide employed should be as active as possible. It should, therefore, preferably be precipitated at temperatures not higher than 20–30°C and the excess of caustic soda or ammonium should be as small as possible. The correct product has a deep reddish brown color, while the less active ferric hydroxide has a much lighter shade and may even be cream colored.

It will be clear to those skilled in this art that other metal hydroxides may be substituted in whole or part for the ferric hydroxide. Similar hydroxides tend to act in a similar way. Investigations show, for example, that mixtures of the hydrates of nickel, cobalt and manganese may be similarly employed.

This application is a continuation in part of our copending application Serial No. 297,054, filed September 29, 1939, now abandoned.

We claim:
1. In the electrolytic refining of nickel, in which the impure nickel electrolyte, containing a limited amount of iron in solution, coming from the electrolytic cell is subjected to cementation and neutralization with nickel until the electrolyte is only slightly acid to remove the greater part of such impurities as copper and arsenic; the solids are separated from the electrolyte, the electrolyte is aerated to precipitate practically all of the iron as ferric hydroxide, which carries with it a substantial amount of the impurities lead, arsenic and copper; the electrolyte before it is aerated contains substantially no more iron in solution than can be precipitated solely by the aeration;
and the acidity of the electrolyte is insufficient to dissolve the ferric hydroxide so formed: the improvement which comprises subjecting the purified nickel electrolyte to the additional purifying action of ferric hydroxide especially prepared outside of the electrolyte by wet precipitation, the ferric hydroxide being introduced while still wet from the precipitation into the electrolyte in amount sufficient to adsorb thereon a substantial amount of the remaining impurities lead, arsenic and copper, the acidity of the electrolyte being insufficient to dissolve the ferric hydroxide, separating the ferric hydroxide and its adsorbed residual impurities from the electrolyte, and subjecting the electrolyte thus purified to electrolysis to produce nickel cathodes of high purity.

2. Method according to claim 1, in which the specially added ferric hydroxide and its adsorbed impurities are removed by filtering, re-pulping the filter cake containing the added ferric hydroxide and adsorbed impurities with a small amount of nickel electrolyte, and returning the admixture to the main body of electrolyte about to be purified in accordance with the preceding claim so that the remaining adsorptive capacity of the added ferric hydroxide present in the filter cake is utilized to adsorb further amounts of impurities.

ANTON MARTIN GRONNINGSAETER.
BERTIN G. HOMMERN.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,163,286</td>
<td>Vadner</td>
<td>Dec. 7, 1915</td>
</tr>
<tr>
<td>1,887,037</td>
<td>Peek et al.</td>
<td>Nov. 8, 1932</td>
</tr>
<tr>
<td>1,986,967</td>
<td>Gronningsaeter</td>
<td>Jan. 8, 1935</td>
</tr>
<tr>
<td>2,066,347</td>
<td>Gronningsaeter</td>
<td>Jan. 5, 1937</td>
</tr>
</tbody>
</table>

OTHER REFERENCES