

## UNITED STATES PATENT OFFICE

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METHOD FOR PRODUCTION OF MALLEABLE  
AND ANNEALABLE NICKEL DIRECT BY  
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## 1 Claim. (Cl. 204—14)

In electrolytic metal refining the metal obtained is usually resmelted before passing through the further operations necessary to turn out a finished product. It is evident that it is desirable to produce the metal in such form and with such properties that this resmelting and part of the further fabricating work on the smelted material can be omitted. It is a generation since experiments were started with direct production of copper pipes and copper sheets by electrolysis, but only very recently has such manufacture of copper sheets reached any importance. Experiments which have been made with production of iron pipes by electrolysis have so far not reached commercial importance.

Nickel sheets (and pipes) are now made by smelting nickel to ingots which are mechanically worked, in a way similar to that for iron, into sheets, pipes, wire, etc., a procedure involving quite considerable expense, because nickel is not easy to work. It has also been proposed to produce nickel direct by electrolysis, which, without resmelting and easier than with ingots produced by smelting, can be worked into sheets, etc. Particularly in late years, when the nickel electrolysis has come under much closer control than before, considerable experimenting has taken place in this field, but the results obtained have not gained any considerable practical importance. The reason for this is partly the high extra costs for production, and partly the uncertain and less satisfactory technical results. For the experiments made, nickel as a rule has been resmelted and used as anodes in a bath, where under special conditions a malleable nickel has been deposited; this, as will be seen, is no attempt to get a satisfactory product from nickel produced direct as a step in the refining process proper. Partly, it has also been assumed that the use of rotating cathodes would be necessary; under such conditions the extra costs would of course be comparatively high.

The aim of the present invention has been to find a method by which it is possible in connection with the refining process to obtain a product which is suitable for further mechanical working. The method permits production of nickel sheets of approximately the dimensions desired. It is therefore only necessary to give these a quite simple rolling treatment in order to get the desired exact dimensions, and in order to get a satisfactory surface. The sheets obtained are, after annealing, if desired, ready for the trade. A product for the trade is therefore ob-

tained by a very simple rolling operation, followed if desired by annealing.

The requirements for a satisfactory product are the following:

The material for the trade must not only be malleable, but must also after possible annealing have the mechanical properties that are necessary for further fabricating operations. Further, the surface of the finished product must satisfy the demands of the trade. Hitherto, it has been difficult with certainty to make a material which after annealing satisfies the demands of the users as to strength and ability to stand mechanical working. Furthermore, the nickel produced has had a tendency during the electrolytic deposition to form growths on the surface thus spoiling the same. The difficulties have been overcome by proper attention during the production of the nickel to the factors described in the following:

Of decided importance for obtaining the results desired is that the deposition of nickel takes place under such conditions that a nickel of extraordinary purity is deposited. Harmful impurities are metals, as for instance, arsenic and lead. Other impurities possibly even worse are organic matter, hydrogen and mechanically occluded hydroxides, basic salts, and electrolyte; in short all substances which by annealing destroy the structure of the metal. The special purity of the nickel may conveniently be obtained by using a process as described in my copending applications Serial Nos. 487,369, filed October 8, 1930 and 685,226, filed August 15, 1933 by which process the electrolyte is first treated with gas reduced nickel to precipitate copper, and to neutralize free acid, thereafter blown with air to precipitate iron by oxidation and hydrolysis, and then passed through an electrolytic purification process whereby the largest part of the remaining metallic impurities are deposited with, and concentrated in a small amount of the nickel, and perhaps finally blown further with air for complete precipitation of iron. After this treatment, the electrolyte may be used for the deposition of a larger amount of nickel, which according to this method may have a very high purity so far as the metallic impurities are concerned. This purification operation also tends to remove organic matter. As to hydroxides, basic salts and hydrogen, the content in the nickel of these may be controlled by using a pH for the electrolyte suitable for the temperature and current density used. Since the hydrogen content in the electrolytically deposited nickel goes down with increasing pH, the pH should be as high as pos-

sible; but it must on the other hand not be so high that there is a risk of precipitating out hydroxides and basic salts by hydrolysis. Since iron hydrolyzes easily, it is of special importance that the electrolyte used have the lowest possible iron content. It has been found that better results are obtained by using a lower temperature than has heretofore been used for nickel electrolysis. It has for instance been proved that under otherwise identical conditions, the nickel obtained is considerably softer at 40° C. than at 55° C. The reason for this is believed to be that the nickel deposited at lower temperatures contains less hydrogen. By the above mentioned purification process, organic matter is removed both by the electrolytic purification and by the blowing with air to remove iron. In many cases it is favorable to remove organic matter more completely, and this can be done by finally giving a further oxidizing treatment with air, hydrogen peroxide, potassium permanganate, or other oxidizing agents that are not harmful for the later electrolytic deposition of nickel. Without daring to say that a complete explanation of the phenomena has been given, it can be stated that by a method as described a malleable metal may be obtained which can stand annealing and still retain satisfactory mechanical properties.

Another main difficulty to overcome in the manufacture is growths on the electrolytically deposited nickel. While unevenness on the surface of the metal, on which deposition has taken place, will show, this is not an important difficulty. The difficulty is in growths on the surface, "berries", which probably has as root a nonmetallic impurity (for instance hydroxide). This difficulty can be overcome by the use of a rotating cathode which is kept clean by, for instance, a rotating rubber cylinder, but this is expensive. I have succeeded by the use of quite clear electrolyte with especially low iron content and using a suitable pH, temperature and current density to produce nickel on stationary cathodes with a sufficiently smooth surface, something of the greatest importance for the economy of the process.

A highly purified nickel electrolyte, containing at best only traces of impurities that work against a malleable and annealable product and a smooth surface, must be employed in the making of the cathodes. As pointed out in said co-pending applications, an acidic nickel-copper electrolyte, containing an objectionable amount of iron in solution, is subjected to the neutralizing and copper-cementing action of finely-divided, highly-reactive, metallic nickel powder obtained by gas reduction at a temperature only slightly above that required to effect reduction. The highly reactive nickel is sufficient in amount and reactivity to effect substantial neutralization of the electrolyte without the introduction of any other neutralizing agent. The electrolyte is filtered to remove copper, arsenic, and accompanying solids. The electrolyte thus neutralized is advantageously subjected to aeration to effect precipitation by oxidation and hydrolysis of substantially all of the objectionable iron present.

In order to purify the electrolyte further, it is preferably subjected 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. Rapid relative movement is advantageously effected between the electrolyte and the cathode during the

preliminary electrolysis so that the impurities, such as copper, arsenic and lead, 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 the impurities on the cathode. The current density and the amount of current employed are regulated to effect neutralization of the electrolyte to such a degree that a small amount of iron still present may be more readily precipitated by oxidation and hydrolysis. The neutralized electrolyte may then be subjected to aeration to effect precipitation of substantially all of the remaining objectionable iron, and filtered to remove the precipitated iron.

It will, of course, be clear to those skilled in this art that any other effective procedure may be employed to remove harmful impurities in order to obtain a highly purified electrolyte, which is required in the practice of the present invention.

The highly purified electrolyte is then subjected to the main electrolysis step in the nickel-refining operation. The temperature and pH value of the electrolyte and the current density are so correlated in relation one to the other as to inhibit the formation of hydroxides and hydrogen. The pH of the electrolyte is maintained substantially as high as possible without precipitation of hydroxides and basic salts of the impurities, including hydroxides and basic salts of nickel, are precipitated by hydrolysis to inhibit the occlusion of hydroxides in the cathodes and to inhibit the formation of berries. The temperature of the electrolyte is preferably maintained within a range of about 25-45° C. A current density is employed that is sufficiently low to inhibit the growth of berries on the cathodes.

A few examples of specific applications of the invention are herewith presented. It will, of course, be understood that they are merely illustrative and that the invention is not to be thereby restricted.

#### Example 1

The process is carried out in connection with the nickel refining process as described in my above mentioned applications. Thereby is obtained a nickel with 99.98+Ni(+Co.). A purification carried to the extreme is not always necessary, but improves the obtained metal's quality. To the electrolyte purified in this way, and filtered, is added a little hydrogen peroxide. Electrolytic deposition takes place on aluminum plates at a temperature of 40° C. and a current density of 1 amp. per dm<sup>2</sup>. At this temperature and current density a pH of 5.4 (determined by the La Motte colorimetric standard) is found favorable.

#### Example 2

A nickel electrolyte is given such a complete purification treatment by known methods that nickel deposited therefrom contains less than 0.01% of arsenic, antimony, tin, bismuth, lead, hydrogen, sulphur, selenium and tellurium combined. Then the electrolyte at 55° C. is given a treatment with potassium permanganate whereby most of its content of organic matter is oxidized away; after filtering and cooling to 25° C., sulphuric acid is added to bring the pH to 5.7. From this electrolyte nickel is deposited at a current density of 0.6 ampere per dm<sup>2</sup>.

#### Example 3

An electrolyte for use for electrodeposition of ordinary nickel is purified by methods described

in the above mentioned applications. A part of this electrolyte, to be used for production of malleable annealable nickel, is given a renewed electrolytic treatment for further removal of copper, arsenic, lead and other metal impurities followed by another oxidation by blowing with air in order to lower further its content of organic matter and iron. The electrolyte is then filtered and sulphuric acid added to regulate the pH to 5.6 and the temperature lowered to 45° C. The iron content of the electrolyte is after this treatment so low that the nickel obtained by the following electrolysis contains less than 0.002% iron.

In the method of producing malleable and annealable nickel cathodes by electrolytic deposition directly from nickel sulfate electrolytes employed in nickel refining operations, the steps which comprise subjecting a highly purified nickel electrolyte, containing traces only of impurities which conventionally are removed, to electrolytic deposition at a temperature of from about 25° C. to 45° C. at a current density not substantially exceeding one ampere per square decimeter, and maintaining the pH of the electrolyte as high as possible without precipitation of hydroxides and basic salts by hydrolysis.

I claim:

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