

Nov. 16, 1948.

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2,453,757

PROCESS FOR PRODUCING MODIFIED ELECTRONICKEL

Filed Aug. 6, 1943

Fig. 1.

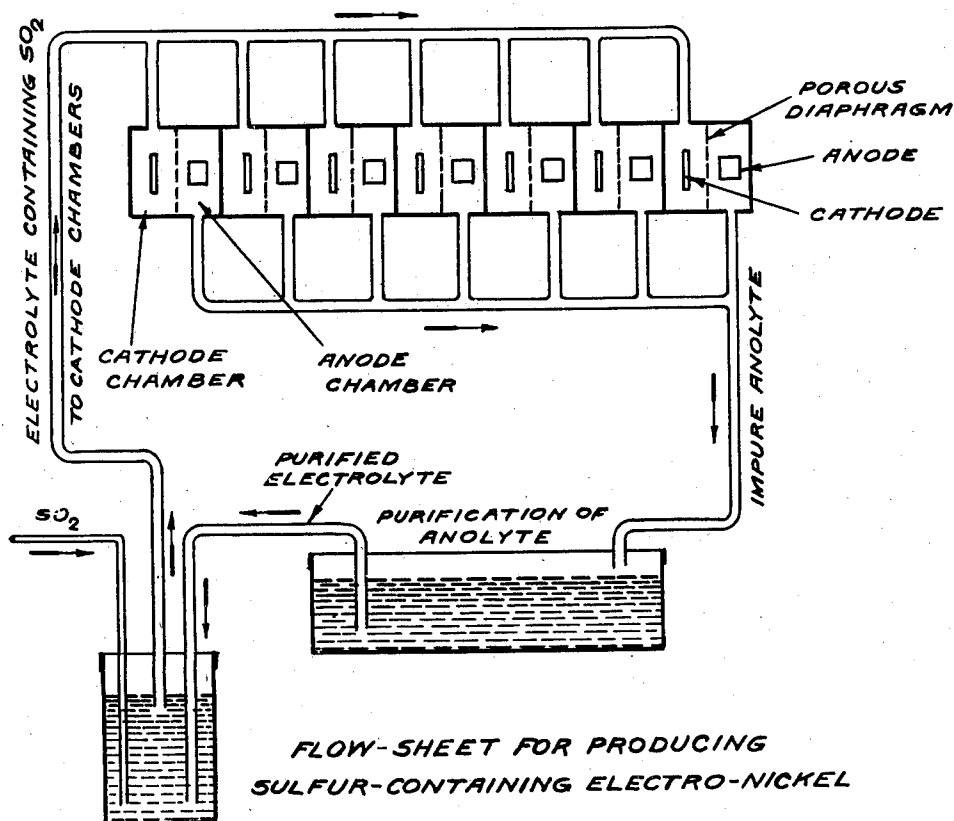
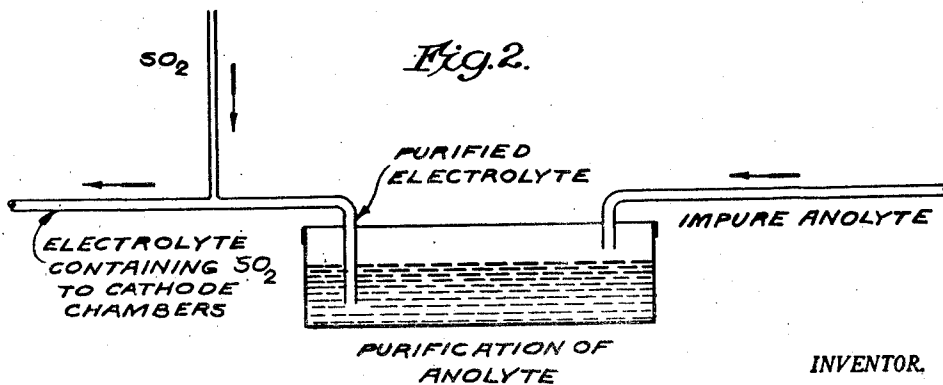


Fig. 2.



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2,453,757

PROCESS FOR PRODUCING MODIFIED
ELECTRONICKEL

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Application August 6, 1943, Serial No. 497,601
In Canada June 12, 1943

4 Claims. (Cl. 204—37)

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The present invention relates to the production in situ of electro-deposited nickel containing sulfur and, more particularly, to the production in situ of electro-deposited nickel containing sulfur and suitable for use as anode in the electroplating of protective and/or decorative coatings of nickel electro-plate.

Since nickel electro-plating was first employed for production of protective or decorative finishes, many metals and some non-metals have been added to the nickel as a result of one theory or another. Thus, in the early days, aluminum, iron, lead, zinc and other metals were added to the nickel in order to lower the melting point of the nickel and facilitate casting. In more recent years, such materials as titanium, copper and magnesium have been added to nickel preparatory to casting or casting and rolling anodes for use in electro-plating protective and/or decorative electro-plates of nickel. Sulfur has also been incorporated in nickel for use as electro-plating anodes alone or in conjunction with oxygen. Such a nickel anode is disclosed in the Geiger U. S. Patents Nos. 1,941,256 and 1,941,257. Furthermore, Spencer points out in an article entitled "The Corrosion of Nickel Anodes" published in the Metal Industry (London) January 22, 1937, that magnesium or manganese should be present in anodes containing sulfur in order that the sulfur will combine to form a manganese or magnesium sulfide to the exclusion of nickel sulfides. In this article Spencer points out that nickel sulfide is insoluble in the plating solution and that when the major portion of the sulfur is combined with the nickel, the metallic nickel grains dissolve and leave the sulfide in veins on the surface or in detached particles which float across the bath and even lodge on the cathode to cause rough deposits.

In a recent U. S. patent granted to Bleber and Tschop, No. 2,304,059, for "Nickel anodes," these patentees pointed out the necessity for providing a nickel anode having a critical coordinated relationship between the addition elements carbon, silicon, magnesium and sulfur. These patentees likewise point out that in the absence of sufficient magnesium to combine with substantially all of the sulfur, nickel anodes containing sulfur corrode in a non-uniform manner with the produc-

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tion of excessive amounts of sludge and loose nickel.

From the foregoing it is manifest that the art has been provided with a large variety of fused nickel anodes for use in the electro-plating of protective and/or decorative electro-plates of nickel and that various hypotheses exist which form a basis for the addition of the various addition elements. However, the investigations of the last five years have clearly shown that while sulfur is an excellent agent for increasing the corrosion of nickel anodes and for enhancing the uniformity of corrosion and the activity of nickel anodes at high pH, such as pH 4 to 5.5 (Q), nevertheless the experts in the art are agreed that free sulfur is detrimental and that magnesium or manganese should be present in amounts sufficient to bind substantially all of the sulfur as sulfide. It is to be noted that while Spencer suggests that manganese may be substituted for magnesium in order to overcome the detrimental effects of free sulfur, most electro-platers hold that in the presence of manganese unsatisfactory nickel electro-plates are obtained. As a consequence, most specifications relating to the composition of nickel anodes for the electro-plating of protective and/or decorative coatings, place a limit of about 0.001% as the upper limit for manganese in a satisfactory nickel anode.

As has been pointed out in the Geiger U. S. Patent No. 2,274,056, granted February 24, 1942, "Extruded anode," there are a minimum of 9 to 10 operations in producing a rolled anode. As a consequence, the electro-plater has always felt that if a satisfactory nickel anode could be produced directly in the operation of electro-refining nickel, desirable economies could be effected which could be passed on to the electro-plater. Consequently, there has been a demand in the art for electro-deposited nickel in the unfused condition in a form to provide satisfactory activity at high pH, such as pH 4.0 to 5.5 (Q), smooth corrosion and the production of small amounts of sludge and loose nickel.

Attempts have been made to employ conventional electrolytic nickel as anode in electro-plating nickel finishes. Many experts in the art in the last ten to fifteen years have attempted to use conventional electrolytic nickel as anode, but except when used in baths operating at relatively

low pH, such as pH 1.5 to 2.0 (Q), i.e., highly acid baths, anodes of conventional unfused electro-nickel have proved unsatisfactory.

In 1936 Raub published an article in *Mitteilungen des Forschungsinstituts und Probenamts für Edelmetalle* in which he outlined some of the difficulties German electro-platers encountered in attempting to circumvent the conditions arising from a lack of metallic nickel. The German electro-platers had used insoluble anodes such as carbon, lead and stainless steel and had found each of them unsatisfactory or as Raub states the situation:

"The use of insoluble anodes for the saving of nickel may also in view of all previous experiences be only an emergency measure the use of which is permissible only under most urgent compulsion."

This foreign authority on nickel anodes for electro-plating mentions a process developed by the Langbein Pfanhauser Werke Leipzig in which the relatively readily obtainable nickel salts are used as a source of nickel for the production of nickel plated anodes which, in turn, may be used in the electro-plating of protective and/or decorative coatings of nickel. Raub condemns these anodes which are essentially conventional unfused electrolytic nickel as only slightly better than insoluble anodes. In addition to the condemnation by this foreign expert, Spencer likewise condemns the use of conventional prior art electro-nickel as an anode in the production of protective and decorative electro-plates. In the article to which reference has been made hereinbefore, Spencer makes the following statements:

"The pure nickel used in industry in the United States is supplied in the form of electro-deposited plates or sheets about one-fourth inch in thickness and cut up in squares of suitable size. It has the typical structure of such deposits in that it consists of groupings of parallel elongated crystals, their size and shape apparently being dependent on the uniformity or non-uniformity of the electric current, composition of the solution, temperature, and other such factors. Any change in these will alter the rate of deposition and the crystal size. If the current is stopped, metal deposition will cease, and re-solution of nickel from the cathode may occur, or copper or other metal impurities in the solution may deposit by immersion with the formation of a film of oxides or basic salts on the surface. When deposition is resumed, a new layer of crystals of different orientation will be formed, probably with weak adherence to the underlying metal. This is one reason why cathode sheet nickel would be unsatisfactory for use as anodes.

"* * * Cathode sheet nickel, provided it could be electro-deposited in long, narrow sheets of sufficient thickness and without separate layers of metal, should be suitable for use as anodes in a well-balanced plating solution. Because of the internal stresses developed in deposition, it should be more easily attacked by solution than annealed or heat-treated metal. On the other hand, since the stresses probably are not uniform throughout the piece, the corrosion would be uneven, and an undesirable amount of anode scrap would be formed with a considerable quantity of loose metallic particles which would interfere with smooth plating. It would seem, therefore, that cathode sheets should be given a slight annealing treatment in order to relieve such stresses and produce a metal as uniform in grain size as

possible. From a commercial point of view it is questionable whether the cost of depositing such an anode and annealing it would be low enough to make it economically practicable."

From the foregoing it is apparent that this expert in the art discounts entirely the possibility that cathode nickel could be used as an anode in the electro-deposition of decorative and/or protective coatings of nickel. Furthermore, it will be noted that this expert in the art bases his opinion that electro-nickel will not provide a satisfactory anode upon characteristics of electro-nickel, i. e., internal stresses, which are in no way related to the chemical composition of the anode.

Tests of Spencer's suggestion have proven that prior art cathode nickel substantially devoid of sulfur, i. e., containing less than 0.005% sulfur, when annealed in accordance with Spencer's suggestion as disclosed in the prior art, shows little or no improvement in corrosion properties as anodes in nickel electroplating baths over un-annealed electro-nickel of the same composition. Furthermore, an annealing and quenching treatment most recently disclosed in the Hull U. S. Patent No. 2,297,766 is not entirely satisfactory. That is to say, the annealing and quenching treatment disclosed in the aforesaid Hull patent raises the limit of activity of electro-nickel from pH 2.5 (Q.) for normally sulfur-free electro-nickel to pH 3.5 (Q.) for electro-nickel treated in accordance with the Hull disclosure. At pH values higher than 3.5 (Q.) electro-nickel treated in accordance with the Hull process produces larger amounts of loose nickel than untreated electro-nickel when used as anode in nickel electroplating baths.

Thus it is manifest that the electro-plating art had found cast and rolled anodes of fused nickel satisfactory from a technical aspect in many instances, but sought a cheaper source of nickel anodes. It is also readily recognized that the art had not found prior art conventional unfused electro-nickel suitable for use as anode in the slightly acid range of pH 3 to pH 5.5 (Q.) even when annealed. In addition, experts in the art have condemned electro-nickel as anode for reasons entirely disconnected from the chemical composition of electro-nickel. However, it has been discovered that satisfactory electro-nickel or cathode nickel anodes can be produced in situ during the electro-refining of impure nickel.

It is an object of the present invention to provide a process for producing electro-nickel or cathode nickel in situ which is satisfactory for use as anode in the electro-plating of protective and/or decorative electro-plates of nickel.

It is another object of the present invention to provide cathode nickel containing a critical amount of sulfur produced in situ without fusion for use as anode in the electro-plating of protective and/or decorative electro-plates of nickel in baths having a pH more alkaline than pH 2 (Q.)

It is a further object of the present invention to provide a process for producing electro-nickel or cathode nickel containing copper and sulfur and suitable for use as anode without fusion in electro-plating protective and/or decorative electro-plates of nickel.

It is also within the scope of the present invention to provide a process for producing electro-nickel or cathode nickel containing a minimum amount of sulfur which after heat treatment is suitable for use as anode in electro-plating pro-

tective and/or decorative electro-platings of nickel from baths having a pH more alkaline than pH 2 (Q.).

The present invention also contemplates the production of heat-treated electro-nickel or cathode-nickel containing sulfur.

It is also within the contemplation of the present invention to provide cathode nickel or electro-nickel containing copper and sulfur.

The present invention also provides for the production of electro-nickel or cathode-nickel containing carbon, copper and sulfur.

Other objects and advantages will become apparent from the following description taken in conjunction with the drawings in which:

Figure 1 is a more or less diagrammatic flow sheet illustrative of the application of the principles of the present invention to the production of modified cathode nickel or electro-nickel; and

Figure 2 is illustrative in a more or less diagrammatic manner of another embodiment of the application of the principles of the present invention to the production of modified cathode nickel or electro-nickel.

Broadly speaking, the novel modified electro-nickel or cathode nickel can be produced by introducing suitable re-agents into the electrolyte of a nickel electro-refining operation. That is to say, whether the electrolyte employed for the electro-refining of nickel be the conventional all-sulfate electrolyte which has been the one most generally employed for this purpose or the all-chloride electrolyte which has not been used to so great an extent, or the novel sulfate-chloride electrolyte disclosed in the co-pending U. S. application Serial No. 472,471, now Patent No. 2,394,874, granted February 12, 1946, the novel modified cathode nickel or electro-nickel can be produced in substantially the same manner by addition of the same re-agents, whether the electrolyte be of the all-sulfate, the all-chloride, or the sulfate-chloride type.

Sulfur can be introduced into electro-nickel or cathode nickel without fusion of the nickel by introducing a sulfur-bearing compound soluble in the electrolyte and reducible to H_2S at the cathode into the purified electrolyte. Illustrative of such addition agents are SO_2 introduced either as a gas or as an aqueous solution thereof, sulfites and acid sulfites of the alkali metals. As those skilled in the art know, a primary consideration in determining what agents may be employed for introducing any material into electro-nickel is the effect of the material upon the purification of the electrolyte. For example, the sodium to nickel ratio in a nickel electro-refining electrolyte must be maintained in a critical proportion in order to avoid producing a brittle electro-nickel. It has been found that a nickel to sodium ratio of about $1\frac{1}{2}$ to 1 provides an electro-nickel having suitable ductility. When the ratio becomes smaller, the electro-nickel becomes quite brittle and when the ratio becomes larger, the electro-nickel becomes more ductile. Consequently in selecting a material to be added to a nickel electrolyte for electro-refining nickel, the operator is confronted with the problem of maintaining this nickel to sodium ratio. In addition to the foregoing, it is necessary that the carrier of the sulfur be of such character that it is either eliminated during the electro-deposition of the sulfur, is readily eliminated before the attempt is made to purify the electrolyte, or does not interfere with the purification of the impure electrolyte. A more comprehensive appre-

ciation of this problem is most readily obtained by a consideration of the conventional process for the production of conventional prior art electro-nickel substantially devoid of sulfur.

The most generally practiced method for electro-refining nickel involves the use of an all-sulfate electrolyte. The process as usually carried out involves the use of a cell having a diaphragm separating the anode compartment from the cathode compartment. An impure anode is employed and the anolyte removed continuously for purification which involves removal of iron, arsenic, lead and copper. I do not know of any practical method for the continuous removal of cobalt from all-sulfate nickel electrolytes. Various schemes have been recommended, but all of them are extremely difficult to operate and none of them is being used commercially. Removal of the impurities set forth hereinbefore provides a purified electrolyte which is introduced into the cathode compartments of the various cells at such a rate as to maintain a hydrostatic head sufficient to overcome the tendency of the cations, copper, iron, etc., to migrate from the impure anolyte into the relatively highly purified catholyte. In the cathode compartments, a relatively pure nickel is electro-deposited from the purified electrolyte.

The foregoing process as generally employed is described in more detail in the article by R. L. Peek entitled "Refining nickel-copper matte at Port Colborne" in the November 10, 1930, issue of Engineering and Mining Journal, published by McGraw-Hill Book Company, Inc.

Briefly stated, the electro-refining of nickel involves the production of impure nickel anodes which are cast in any suitable manner and generally have a nickel content of about 90% to about 96%. Dependent upon the source of the nickel from which the impure nickel anodes are produced, such anodes will contain greater or lesser amounts of the impurities present in the ore. Thus, for example, in one industrial operation, the impure nickel anodes contain about 94% to about 96% of nickel, about 2.5% to about 3.5% of copper, about 0.7% to about 0.9% of cobalt, about 0.5% to about 1.0% of iron, about 0.002% to about 0.004% of lead, about 0.05% to about 0.07% of arsenic and about 0.5% to about 0.8% of sulfur.

The electro-refining of nickel involves solution of the metallic constituents of the impure anode in the anolyte followed by purification of the anolyte to remove iron, copper, cobalt, lead, arsenic, etc. to obtain a purified electrolyte from which electro-nickel can be produced.

Electrolytic nickel produced in the all-sulfate electrolyte has the following composition:

Composition	Per Cent
Nickel.....	About 99.18 to about 99.29
Cobalt.....	About 0.80 to about 0.70
Copper.....	About 0.005 to about 0.003
Iron.....	About 0.008 to about 0.005
Lead.....	About 0.004 to about 0.002
Arsenic.....	About 0.003 to about 0.002
Sulfur.....	About 0.000 to about 0.0001
Carbon.....	About 0.000 to about 0.000

The general features of the electrolytic cell preferably employed in conjunction with the Hybinette bag are described more or less in detail, together with the process employed in conjunction therewith, in the Hybinette U. S. Patent No. 805,969. In the prior art all-sulfate process, the electro-refining of nickel is generally and preferably carried out employing Hybinette bags. As

those skilled in the art know, the Hybinette bag generally comprises a wooden frame of spruce or the like covered with a canvas of such weight that a slight hydrostatic pressure maintained on the cathode side of the canvas substantially prevents the migration of copper, cobalt, nickel, iron and similar cations from the impure electrolyte through the canvas diaphragm into the purified electrolyte present as a catholyte in the cathode compartment of the cell.

As clearly set forth in U. S. Patent No. 805,969, a hydrostatic pressure is maintained in the cathode compartment and impure anolyte withdrawn from the anode compartment continuously. The impure anolyte is first subjected to purification to remove copper and, in the all-sulfate ion electrolyte, the copper is removed by cementation through addition of nickel, preferably in the form of freshly reduced nickel powder, before the iron, lead and arsenic are removed. After the copper has been removed by cementation, the iron, lead and arsenic are then removed. When desired, the cobalt is removed in the all-sulfate ion electrolyte by the addition of nickel, preferably in the form of an oxide or hydrated oxide prepared outside the electrolyte system by the action of a strong oxidizing agent upon nickelous hydrate, whereby the nickel goes into solution and the cobalt is precipitated.

The refining of nickel-containing material by electro-deposition of nickel from a purified electrolyte involves the use of a number of electrolytic cells employing a diaphragm to separate impure anolyte from the catholyte. The number of cells required is, of course, dependent upon the amount of nickel to be electro-deposited in a unit of time, most of the cells being operated with a soluble anode while a few of the cells are operated employing insoluble anodes. The soluble anodes are obtained, by casting or otherwise forming, from impure metallic material containing a relatively high percentage of nickel and also containing so much of the impurities, copper, iron, cobalt, lead, arsenic and sulfur that the impure anodes are not acceptable, per se, to the trade as pure nickel. The impure anodes are immersed in the anode compartment of the diaphragm cell in contact with lean anolyte obtained from previous operations, i. e., catholyte, the nickel content of which has been suitably lowered by electro-deposition of nickel. Under the influence of the electric current and the anions present in the lean anolyte, the soluble impure anodes are more or less completely dissolved in the lean anolyte with the production of an impure anolyte containing practically all of the nickel and the base metals, copper, cobalt, iron, lead and arsenic. The precious metals, gold, platinum and other metals of the platinum metal group together with sulfides of copper and nickel, present in the soluble impure anodes, remain on the more or less completely dissolved impure anodes as anode slimes in quantities dependent upon previous operations and the source of the nickel.

The process for electro-refining nickel employing a sulfate-chloride electrolyte is somewhat similar to that utilized in electro-refining nickel with an all-sulfate electrolyte. However, there are some differences. Thus, for example, it has been found more satisfactory to remove lead, iron and arsenic from the electrolyte before removing copper. In the sulfate-chloride electrolyte employed in the process disclosed in the co-pending U. S. application Serial No. 472,471, the iron in the impure anolyte is precipitated in the presence

of cupric copper ions by oxidizing the iron with oxygen at a pH which permits the iron to hydrolyze to the hydroxide. Without separating the iron precipitate, arsenic and lead are oxidized with chlorine and then precipitated together with the iron. By suitable control of the pH of the solution, cobalt can likewise be precipitated with the iron, arsenic and lead. Thereafter, the copper is removed in any conventional manner, preferably by cementation using freshly reduced nickel as the agent. In the event that all of the cobalt has not been removed by re-precipitation with iron, arsenic and lead, the residual cobalt is precipitated by the addition of chlorine and nickel carbonate to provide an electrolyte substantially free from iron, lead, arsenic, copper and cobalt.

The purification of the all-chloride electrolyte is carried on in a manner similar to that employed in purifying the all-sulfate electrolyte.

It is preferred in producing the novel modified cathode nickel or electro-nickel to maintain an electrolyte temperature of about 125° F. to about 140° F. and a pH of about 3.5 to about 5.0 (Q.). The lower pH limit of operation is determined by the pH at which sulfide sulfur may be deposited from purified nickel electrolytes containing a sulfur-bearing addition agent such as sulfur dioxide, sodium sulfite, or sodium acid sulfite, or in general an electrolyte soluble sulfur bearing compound capable of reduction to H₂S at the cathode. This value is determined by the solubility product of nickel sulfide under the conditions existing at the cathode. Lower pH values may be employed by adding ions capable of forming sulfides having a lower solubility than nickel sulfide to the electrolyte. Sulfur-bearing cathode nickel or electro-nickel has been produced from an all-sulfate nickel electrolyte containing 42 grams per liter of nickel, 40 grams per liter of sodium sulfate and 20 grams per liter of boric acid at pH 4.8 and a temperature of 130° F. from anodes containing the impurities copper and iron. Preferably, the sulfur-bearing addition agent is added to the purified electrolyte before introduction into the cathode compartment in such a manner as to ensure uniform distribution of the sulfur-bearing material throughout the electrolyte flowing to the cathode cell. Thus, for example, the sulfur-bearing material may be introduced into the electrolyte immediately after the last purification step or the purified electrolyte may be introduced into a holding tank and the sulfur-bearing compound likewise added to the electrolyte in the holding tank. On the other hand, the holding tank may be eliminated and the sulfur-bearing compound introduced into the stream of purified electrolyte a suitable distance before the purified electrolyte enters the cathode compartments.

While the sulfites and acid sulfites of the alkali metals or even the alkaline earth metals may be employed, it is preferred to use gaseous sulfur dioxide or an aqueous solution of sulfur dioxide. Sulfur dioxide is the preferred addition agent because it can be readily removed from the impure anolyte by aeration and thus its effect upon the purification of the impure anolyte readily overcome. In addition the reaction products are not harmful and no additional cations are introduced into the electrolyte which may either affect the balance of the electrolyte or interfere with the purification thereof.

It has been found that the sulfur content of cathode nickel or electro-nickel produced in accordance with the principles of the present invention has a relation to the concentration of the

sulfur-bearing material present in the electrolyte in the cathode chamber. Thus, it is apparent from the following tabulation that the sulfur content of electro-nickel or cathode-nickel expressed in percent is substantially equivalent to the amount of SO_2 present in the electrolyte expressed as grams per liter.

Cathode No.	Grams Per Liter SO_2 In Purified Catholyte	pH	Per Cent Sulfur in Electro-Nickel
1-----	0.00	5.0	About 0.000 to about 0.000
2-----	0.04	4.5	About 0.035 to about 0.04
3-----	0.075	4.2	About 0.070 to about 0.08
4-----	0.15	3.8	About 0.10 to about 0.15
5-----	0.18	3.5	About 0.15 to about 0.20
6-----	0.21	3.2	About 0.20 to about 0.22
7-----	0.34	2.9	About 0.30 to about 0.35

Electro-nickel or cathode-nickel produced as above described by introducing a sulfur-bearing compound such as sulfur dioxide or the sulfites or acid sulfites of the alkali metals or alkaline earth metals under an otherwise normal operating condition of temperature and current density is satisfactory for use directly without fusion as anodes when the sulfur-content of the electro-nickel or cathode-nickel is about 0.03 to about 0.5%. When the electro-nickel is corroded in a standard hot Watts bath, the electro-nickel is active throughout the range of pH about 1.5 to pH about 5.5 (Q.). In addition, the electro-nickel corrodes uniformly and what is of greater importance does not produce an amount of sludge or loose nickel appreciably in excess of that which experience has proven is the maximum amount which can be tolerated in industrial electro-plating of protective and/or decorative films of nickel.

Electro-nickel containing 0.005% to 0.03% sulfur may also be rendered satisfactory for use without fusion after undergoing heat treatment at temperatures of about 1500° F. to about 1800° F. for periods of time of about 20 minutes to about 30 minutes in a non-oxidizing, i. e., neutral or reducing atmosphere. After such heat treatment the electro-nickel has substantially the same corrosion properties as electro-nickel containing 0.03 to 0.5% of sulfur, e. g., the annealed electro-nickel corrodes actively at pH 5.5 in distinct contrast to prior art sulfur-free electro-nickel annealed in accordance with prior art process such as that taught by Spencer and Hull to which reference has been made hereinbefore. Although Spencer has suggested that conventional prior art electro-nickel could be made satisfactory for use as anode by some undisclosed annealing treatment, it is to be noted that even when prior art conventional electro-nickel substantially devoid of sulfur is heat-treated as described hereinbefore in conjunction with the novel electro-nickel of the present invention, the so heat-treated prior art electro-nickel substantially devoid of sulfur, i. e., containing no sulfur or less than about 0.005% sulfur, nevertheless does not have satisfactory anode corrosion characteristics and even after such heat-treatment prior art conventional electro-nickel substantially devoid of sulfur is not satisfactory for use as anode because it is not active throughout the range of pH about 1.5 to pH about 5.5 (Q.).

Electro-nickel containing sulfur in excess of 0.03% is somewhat brittle and presents some difficulty in shearing although it is satisfactory for use directly without fusion. This difficulty may be overcome by growing the cathodes to the

desired size and thus eliminating the necessity of shearing. It has been discovered that this tendency to brittleness or the tolerance for sulfur of electro-nickel can be overcome. When copper is added to electro-nickel and correlated to the amount of sulfur present therein electro-nickel containing sulfur in excess of 0.03% sulfur can be produced which not only has all the desirable anode corrosion characteristics, but in addition has a satisfactory ductility in the unannealed condition. In the presence of about 0.01% to about 0.10% copper, the sulfur content of cathode nickel can be raised to as much as 0.12% to provide electro-nickel which is satisfactory for use as anode in the unannealed and unfused condition throughout the pH range of about 1.5 to about pH 5.5 (Q.) and in addition the electro-nickel has practically no tendency to brittleness and may be readily sheared into sizes suitable for use as anode.

The copper-bearing modified electro-nickel containing sulfur may be produced in a manner quite analogous to that described hereinbefore for the production of modified electro-nickel containing sulfur. That is to say, an electrolyte soluble copper salt, such as copper sulfate or copper-chloride or a copper compound, which when introduced into the electrolyte is converted to a soluble form, is added to the electrolyte in carefully controlled amounts sufficient to provide an amount of copper within the range of about 0.001 to about 0.03 gram per liter of electrolyte. The copper compound may be introduced simultaneously with the sulfur-bearing compound or may even be introduced as a copper sulfite. In other words, a solution of copper sulfate, for example, may be introduced into the electrolyte after the final purification thereof wherein the electrolyte has been freed from such impurities as iron, lead, arsenic, copper and cobalt, or the copper salt or the copper compound may be introduced into a holding tank together with sulfur dioxide as indicated hereinbefore. Furthermore, although somewhat more difficult to control, the removal of copper from the impure electrolyte may be regulated to leave in the purified electrolyte a residual amount of copper within the critical limits set forth hereinbefore. In other respects the production of copper-bearing modified electro-nickel containing sulfur is carried out under the same conditions as those employed to produce modified electro-nickel containing sulfur, but substantially no copper.

It has been found that the tolerance of electro-nickel for sulfur can be increased by introducing into the electro-nickel a controlled amount of carbon in addition to a controlled amount of copper. That is to say, electro-nickel containing about 0.02% carbon, 0.15% copper, and about 0.12% sulfur can be produced in an all-sulfate electrolyte or an all-chloride electrolyte or a mixed sulfate-chloride electrolyte by introducing into the electrolyte acetylene as well as a copper salt and a source of sulfur capable of being reduced to H_2S at the cathode. The acetylene is introduced into the electrolyte in amounts sufficient to provide a concentration of about 0.001 to about 0.003 gram of acetylene per liter of electrolyte. Simultaneously, provision is made to provide about 0.03 to about 0.05 gram per liter of copper and about 0.1 to about 0.15 gram of SO_2 per liter of electrolyte. The temperature, current density and pH of the electrolyte during electro-deposition of the carbon-copper-bearing modified electro-nickel contain-

ing sulfur are substantially the same as the values for these variables during the electro-deposition of conventional prior art electro-nickel substantially devoid of sulfur and carbon.

The drawings, Figs. 1 and 2, are believed to be self-explanatory. The drawing in Fig. 1 is illustrative in a more or less diagrammatic manner of the flow of anolyte or impure electrolyte through the various operations whereby the anolyte or impure electrolyte is purified to remove impurities such as iron, arsenic, lead, copper and cobalt to provide purified electrolyte or catholyte. The purified electrolyte, according to the modifications of the present invention illustrated by the drawing in Fig. 1, is introduced into the holding tank and sulfur dioxide in gaseous form or as an aqueous solution thereof likewise introduced into the holding tank. The purified electrolyte containing about 0.005 to about 0.5 gram per liter of SO_2 is then introduced into the cathode compartment or chamber of the electro-refining cells wherein the nickel in the purified electrolyte together with the sulfur of the sulfur dioxide contained therein is deposited at the cathode to provide the novel modified electro-nickel or cathode-nickel described herein. As has been pointed out hereinbefore, sulfur-bearing compounds capable of reduction to H_2S at the cathode, such as sulfites, acid sulfites of the alkali metals and alkaline earth metals may be employed with equally satisfactory results in the place of sulfur dioxide provided the concentration of the sulfite or acid sulfite is controlled to provide a concentration of SO_2 in the purified electrolyte or catholyte equivalent to that set forth hereinbefore. In the production of novel copper-bearing modified electrolytic nickel containing sulfur, the copper salt or other copper compound which is introduced into the purified electrolyte or catholyte may likewise be added to the electrolyte in the holding tank. Similarly, the purified electrolyte or catholyte may be treated with acetylene in the holding tank when it is desired to provide a modified carbon-bearing electro-nickel. Accordingly, it will be understood that when it is desired to produce novel carbon-copper bearing modified electro-nickel or cathode-nickel, the materials which are the source of carbon, copper and sulfur may all be added to the purified electrolyte or catholyte in the holding tank, or when desirable one or more of the addition agents may be added prior to or subsequent to passage of the purified electrolyte through the holding tank, and the remaining addition agent added to the purified electrolyte or catholyte in the holding tank.

Fig. 2 is illustrative of another method of introducing addition agent into the purified electrolyte or catholyte. As is manifest in the embodiment of the present invention illustrated by the drawing (Fig. 2) no holding tank is employed and the addition agents are introduced directly into the stream of purified electrolyte or catholyte. While the drawing illustrates only one point at which the addition agents may be introduced, the addition agents may be introduced at several points provided sufficient time elapses between the time of addition of the last addition agent and introduction into the cathode chamber of the electro-depositing cells to permit thorough mixing of the last addition agent introduced throughout the purified electrolyte or catholyte.

As those skilled in the art know, prior art conventional electro-nickel is produced in an all-sul-

fate electrolyte having a composition within the following limits:

Composition	Grams Per Liter
Nickel.....	About 40 to about 60
SO_4	About 86 to about 126
Boric Acid.....	About 15 to about 30
Na_2SO_4	About 30 to about 40

Temperature of about 130°F . to about 140°F .
pH of about 4.5 to about 5.2 pH (Q.).
Current density of about 10 to about 13 amperes per square foot.

Prior art conventional electro-nickel has been produced in an all-chloride bath having the following composition:

Composition	Grams Per Liter
Nickel.....	About 40 to about 60
Cl	About 50 to about 75
H_2BO_3	About 25 to about 30

Temperature of about 130°F . to about 140°F .
pH of about 4.5 to about 5.2 pH (Q.).
Current density of about 15 to about 20 amperes per square foot.

Prior art conventional electro-nickel substantially devoid of sulfur can be produced in a sulfate-chloride bath having the following composition:

Composition	Grams Per Liter
Nickel.....	About 40 to about 60
SO_4	About 71 to about 120
Cl	About 27 to about 30
Boric Acid.....	About 15 to about 25
Sodium sulfate.....	About 10 to about 35
Sodium chloride.....	About 45 to about 50

As disclosed in the co-pending U. S. application Serial No. 472,471, conventional prior art electro-nickel substantially devoid of sulfur can be produced in the foregoing electrolyte employing:

Temperature of about 130°F . to about 140°F .
pH of about 4.0 to about 5.0 pH (Q.).
Current density of about 15 to about 20 amperes per square foot.

Prior art electro-nickel varies but slightly in composition whether produced in an all-sulfate electrolyte, an all-chloride electrolyte, or a mixed sulfate-chloride electrolyte. Thus prior art conventional electro-nickel produced in an all-sulfate bath generally has a composition as indicated hereinafter:

Composition	Per Cent
Sulfur.....	About 0.000 to about 0.000
Iron.....	About 0.005 to about 0.008
Manganese.....	About 0.001 to about 0.0015
Magnesium.....	About 0.000 to about 0.000
Carbon.....	About 0.000 to about 0.000
Copper.....	About 0.003 to about 0.005
Cobalt.....	About 0.70 to about 0.80
Nickel.....	About 99.18 to about 99.29

Prior art conventional electro-nickel produced in an all-chloride bath generally has a composition within the ranges indicated hereinafter:

Composition	Per Cent
Sulfur.....	About 0.000 to about 0.000
Iron.....	About 0.001 to about 0.001
Manganese.....	About 0.000 to about 0.000
Magnesium.....	About 0.000 to about 0.000
Carbon.....	About 0.000 to about 0.000
Copper.....	About 0.003 to about 0.005
Cobalt.....	About 0.01 to about 0.10
Nickel.....	About 99.98 to about 99.99

Electro-nickel substantially devoid of sulfur and produced in a sulfate-chloride electrolyte, such as described in the co-pending U. S. application Serial No. 472,471 has a composition falling within the range indicated hereinafter:

Composition	Per Cent
Sulfur.....	About 0.000 to about 0.000
Iron.....	About 0.001 to about 0.001
Manganese.....	About 0.000 to about 0.000
Magnesium.....	About 0.000 to about 0.000
Carbon.....	About 0.000 to about 0.000
Copper.....	About 0.003 to about 0.005
Cobalt.....	About 0.01 to about 0.10
Nickel.....	About 99.98 to about 99.99

The novel modified electro-nickel containing sulfur has a composition falling within the range indicated hereinafter:

Composition	Per Cent
Sulfur.....	About 0.005 to about 0.5
Iron.....	About 0.001 to about 0.005
Manganese.....	About 0.000 to about 0.0015
Magnesium.....	About 0.000 to about 0.000
Carbon.....	About 0.000 to about 0.000
Copper.....	About 0.003 to about 0.005
Cobalt.....	About 0.01 to about 0.80
Nickel.....	About 99.81 to about 98.59

Copper-bearing modified electro-nickel containing sulfur has a composition falling within the following range:

Composition	Per Cent
Sulfur.....	About 0.10 to about 0.15
Iron.....	About 0.001 to about 0.005
Manganese.....	About 0.000 to about 0.0015
Magnesium.....	About 0.000 to about 0.000
Carbon.....	About 0.000 to about 0.000
Copper.....	About 0.05 to about 0.15
Cobalt.....	About 0.01 to about 0.80
Nickel.....	About 99.84 to about 98.59

Carbon-copper bearing modified electro-nickel containing sulfur has a composition falling within the range indicated hereinafter:

Composition	Per Cent
Sulfur.....	About 0.10 to about 0.15
Iron.....	About 0.001 to about 0.005
Manganese.....	About 0.000 to about 0.0015
Magnesium.....	About 0.000 to about 0.000
Carbon.....	About 0.01 to about 0.04
Copper.....	About 0.05 to about 0.15
Cobalt.....	About 0.01 to about 0.80
Nickel.....	About 99.83 to about 98.85

When the symbol "(Q.)" is used herein in connection with pH values, it denotes that the pH value is determined with the well known and standard Quinhydrone electrode.

Although the present invention has been described in conjunction with certain preferred embodiments thereof, those skilled in the art will understand that variations and modifications thereof can be made. Such variations and modifications are to be considered within the purview of the application and the scope of the claims.

I claim:

1. A process for producing electro-nickel having good activity as anode up to pH 5.5 (Q.) in nickel electro-plating baths and corroding as anode at pH up to 5.5 (Q.) without the production of undesirable amounts of loose nickel and sludge, which comprises purifying an electrolyte containing nickel and at least one of the group of impurities consisting of copper, iron, arsenic and lead to obtain a purified electrolyte substantially

devoid of said impurities, positively introducing an effective amount of an electrolyte-soluble sulfur-bearing compound selected from the group consisting of sulfur dioxide and sulfites and acid sulfites of the alkali metals and alkaline earth metals into said purified electrolyte, electro-depositing nickel from said purified electrolyte to obtain electro-nickel containing about 0.005% sulfur to about 0.03% sulfur, and subjecting said electro-nickel to heat treatment at temperatures of about 1500° F. to about 1800° F. in a non-oxidizing atmosphere.

2. A process for producing electro-nickel having good activity as anode up to pH 5.5 (Q.) in nickel electro-plating baths and corroding as anode at pH up to 5.5 (Q.) without the production of undesirable amounts of loose nickel and sludge, which comprises purifying an electrolyte containing nickel and at least one of the group of impurities consisting of copper, iron, arsenic and lead to obtain a purified electrolyte substantially devoid of said impurities, positively introducing an effective amount of an electrolyte-soluble sulfur-bearing compound selected from the group consisting of sulfur dioxide and sulfites and acid sulfites of the alkali metals and alkaline earth metals into said purified electrolyte, electro-depositing nickel from said purified electrolyte to obtain electro-nickel containing about 0.005% sulfur to about 0.03% sulfur, and subjecting said electro-nickel to heat treatment at temperatures of about 1500° F. to about 1800° F. in a non-oxidizing atmosphere for about 20 minutes to about 30 minutes.

3. A process for producing electro-nickel having good activity as an anode in nickel electro-plating baths and corroding smoothly up to about pH 5.5 without the production of undesirable amounts of loose nickel and sludge which comprises anodically corroding impure nickel to obtain an electrolyte contaminated with copper and iron, removing said copper and iron by cementation and hydrolysis, respectively, to secure a purified electrolyte, mixing about 0.005 to about 0.03 gram per liter of sulfur dioxide as a saturated aqueous solution thereof with said purified electrolyte, electrodepositing a nickel cathode containing about 0.005 to about 0.03% sulfur from the thus-treated solution, and annealing said nickel cathode for a period of about 20 minutes to about 30 minutes at a temperature of about 1500° F. to about 1800° F. in a reducing atmosphere, the annealed nickel cathode being suitable for subsequent use as an anode.

4. A process for producing electro-nickel having good activity as an anode in nickel electro-plating baths and corroding smoothly up to about pH 5.5 without the production of undesirable amounts of loose nickel and sludge which comprises corroding impure nickel as anode to obtain an electrolyte contaminated with copper and iron, removing said copper and iron by cementation and hydrolysis, respectively, to secure a purified electrolyte, mixing an amount of an electrolyte-soluble sulfur-bearing compound selected from the group consisting of sulfur dioxide and sulfites and acid sulfites of the alkali metals and alkaline earth metals to provide a concentration equivalent to about 0.005 to 0.03 gram per liter of sulfur dioxide with said purified electrolyte, electrodepositing a nickel cathode containing about 0.005 to 0.03% sulfur from the thus-treated solution, and annealing said nickel cathode for a period of about 20 minutes to about 30 minutes at a temperature of about 1500° F. to about 1800° F.

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F. in a reducing atmosphere, the annealed nickel cathode being suitable for subsequent use as an anode.

LOUIS SECONDO RENZONI.

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Certificate of Correction

Patent No. 2,453,757.

November 16, 1948.

LOUIS SECONDO RENZONI

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 7, line 17, for "electroylte" read *electrolyte*; line 44, for "sufur" read *sulfur*; column 9, line 22, for the word "sulfurdioxide" read *sulfur dioxide*; column 12, line 33, in the table, first column thereof, for "Cl" read *Cl-*; column 14, line 13, claim 2, for "electrol-nickel" read *electro-nickel*; line 47, claim 3, before "nickel" strike out "a";

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 29th day of March, A. D. 1949.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.