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PROCESS FOR PRODUCING MODIFIED ELECTRONICKEL

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The present invention relates to a process for the production in situ of electrodeposited nickel containing sulfur, and more particularly, to an improved process for the production in situ of electrodeposited nickel containing sulfur and suitable for use as anode in the electroplating of protective and/or decorative coatings of nickel.

The electroplating art has found that cast and rolled anodes of fused nickel are generally satisfactory from a technical aspect. However, fused nickel anodes require many manufacturing operations in preparing the finished product and fused nickel anodes are comparatively expensive. The art has attempted to employ electrolytic nickel anodes in the protective and/or decorative plating of nickel, but the use of ordinary electrolytic nickel anodes is attended with considerable difficulty because of the poor activity of these anodes. As far as I know, no one at the present time is able to use ordinary electrolytic nickel anodes directly in place of fused nickel anodes without previous extensive revision of the electroplating operation. Furthermore, to my knowledge, prior art processes for producing electrolytic nickel modified to permit its use directly as anode in commercial nickel plating operations have involved the incorporation in the electrolyte used in producing said electrolytic nickel of modifying agents which rendered said electrolyte unsuitable for use in the production of regular electro-refined nickel required to be devoid of said modifying agents. Thus, prior art processes adapted to produce modified electrolytic nickel anodes have suffered severe practical disadvantages from the standpoint of the manufacture of high purity electrolytic nickel.

It has now been discovered that electronickel or cathode nickel anodes satisfactory for use directly as anodes in commercial nickel plating operations can be produced in situ during the commercial electro-refining of impure nickel.

It is an object of the present invention to provide a process for producing electronickel or cathode nickel in situ which is satisfactory for use as anode in the electroplating of protective and/or decorative electroplates 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 electroplating of protective and/or decorative electroplates 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 electronickel

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or cathode nickel containing copper and sulfur and suitable for use as anode without fusion in electroplating protective and/or decorative electroplates of nickel.

The present invention also contemplates the production of electronickel or cathode nickel containing sulfur.

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

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

Other objects and advantages will become apparent from the following description.

Broadly stated, the present invention comprises the production of electrolytic nickel containing sulfur in critically controlled amounts between about 0.06% and about 0.5% substantially uniformly distributed therethrough. The process embodying the invention comprises dissolving impure nickel anodically in a nickel electrolyte, purifying the impure nickel-containing electrolyte to remove substantially all iron, copper, arsenic and lead contained therein, introducing into the purified electrolyte about 0.06 to about 0.5 grams per liter of sulfur dioxide and electrodepositing from said purified electrolyte substantially pure nickel while depositing sulfur within the range of about 0.06% to about 0.5% therein. A feature of the invention is that the electrolyte addition agent, dissolved sulfur dioxide, may be readily removed from the electrolyte by aeration, etc., when desired, and the electrolyte may be thereafter employed in the regular production of high purity electrolytic nickel which is substantially devoid of sulfur. Thus, the process of the invention advantageously provides a method of producing sulfur-bearing electronickel using regular production techniques.

Electrolytic nickel or cathode nickel containing amounts of sulfur as described hereinbefore, particularly amounts of sulfur between about 0.06% to about 0.2% obtained by using 0.06 to 0.2 grams per liter of sulfur dioxide in the electrolyte from which the electronickel is deposited, is suitable for use directly (without fusion) as anode in commercial nickel plating baths. When employed as anode in commercial nickel plating baths such as the Watts-type bath, electrolytic nickel containing sulfur and produced according to the present invention exhibits good corrosion characteristics and corrodes actively over a wide range of pH up to about 5.5 (Q.) and over

a wide range of current density, e. g., about 10 to about 100 amperes per square foot.

According to the present invention, electronickel or cathode nickel containing sulfur can be produced by introducing sulfur dioxide into the electrolyte of a nickel electrorefining operation. That is to say, whether the electrolyte employed for the electrorefining 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 my U. S. Patent No. 2,394,874, granted February 12, 1946, cathode nickel or electronickel containing sulfur can be produced in substantially the same manner by addition of controlled amounts of sulfur dioxide thereto. In other words, whether the electrolyte employed be of the all-sulfate, the all-chloride, or the sulfate-chloride type, it has been discovered that sulfur-containing nickel can be produced therefrom.

Suitable electrolytes which may be employed in carrying out the invention to produce electrolytic nickel are aqueous electrolytes containing or comprised essentially of about 40 to about 80 grams per liter of nickel ions introduced into said electrolyte as at least one nickel compound selected from the group consisting of nickel chloride and nickel sulfate, and about 15 to about 30 grams per liter of boric acid. Addition agents selected from the group consisting of sodium sulfate and sodium chloride may be employed in amounts up to about 60 grams per liter, e. g., about 0.01 to about 60 grams per liter. Small amounts of wetting agents, etc. may also be employed in the bath, e. g., about 0.10 to about 0.25 gram per liter. The electrolytes may be operated within the pH range of about 2.0 to about 4.5, and at temperatures within the range of about 100° to about 150° F. Nickel may be electrodeposited from the electrolytes according to the invention at current densities of from about 10 to about 20 amperes per square foot. When the term "all-sulfate electrolyte" is used herein I mean an aqueous electrolyte containing or comprised essentially of about 40 to about 50 grams per liter of nickel ions, about 85 to about 120 grams per liter of sulfate ions, about 30 to about 50 grams per liter of sodium sulfate, about 15 to about 30 grams per liter of boric acid and not more than about 0.02 grams per liter of chloride ion, e. g., about 0.001 to about 0.02 gram per liter. This electrolyte is operated for purposes of the invention at a pH of about 2.0 to about 4.5. When the term "all-chloride" electrolyte is used herein I mean an aqueous electrolyte containing or comprised essentially of about 40 to about 60 grams per liter of nickel ions, about 78 to about 110 grams per liter of chloride ions, about 50 to about 60 grams per liter of sodium chloride and sulfates present in amounts not greater than that usually considered as traces. For purposes of the invention, the all-chloride electrolyte may be operated at pH values within the range of about 2.0 to about 4.5. When the term "sulfate-chloride" electrolyte is used herein I mean an aqueous electrolyte containing about 40 to about 60 grams per liter of nickel ions, about 65 to about 105 grams per liter of sulfate ions, about 30 to about 40 grams per liter of chloride ions, about 15 to about 30 grams per liter of boric acid, and about 15 to about 25 grams per liter of sodium ions introduced into the bath in the form of at least one of the compounds selected from the group sodium chloride and sodium sulfate. For purposes of the invention, the sulfate-chloride electrolyte may be operated at pH values within the range of about 2.0 to about 4.5.

As those skilled in the art know, the most generally-practiced method for electrorefining nickel involves the use of an all-sulfate electrolyte. The process as generally employed is described 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 the McGraw-Hill Book Company, Inc. The general features of the electrolytic cell preferably employed in the process are described in the Hybinette U. S. Patent No. 805,969.

Briefly stated, the process generally involves the anodic dissolution in a cell having a diaphragm separating the anode compartment from the cathode compartment of soluble impure cast nickel anodes generally having a nickel content of about 90% to about 96%. For example, in one industrial operation, the impure nickel anodes contain about 94% to about 96% nickel, about 2.5% to about 3.5% copper, about 0.7% to about 0.9% cobalt, about 0.5% to about 1% iron, about 0.002% to about 0.004% lead, about 0.05% to about 0.7% arsenic, and about 0.5% to about 0.8% sulfur. In the electrolytic cell described in U. S. Patent No. 805,969, wherein a canvas diaphragm is provided between the cathode compartment and the anode compartment, a hydrostatic pressure is maintained in the cathode compartment which substantially prevents migration of copper, cobalt, nickel, iron and similar cations from the impure anolyte through the diaphragm into the purified catholyte. The impure anodes are dissolved electrolytically in the anode compartment, and the resulting impure anolyte is removed from the anode compartment, is purified, and the purified electrolyte is then returned to the cathode compartment of the cell. When the all-sulfate electrolyte is employed, the impure anolyte removed from the anode compartment is first subjected to purification to remove copper by cementation of the copper upon freshly reduced nickel powder. After the copper has been removed by cementation, the iron, lead and arsenic are removed. The purified electrolyte is then returned to the cell as indicated hereinbefore. It is not ordinarily practicable to continuously remove cobalt from all-sulfate nickel electrolytes. When a sulfate-chloride or all-chloride electrolyte is employed in electrorefining nickel, some differences in the purification procedure have been found advantageous. Thus, for example, it has been found more satisfactory to remove lead, iron and arsenic from the electrolyte before removing the copper.

In the sulfate-chloride electrolyte employed in the process disclosed in my U. S. Patent No. 2,394,874, 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 ion to hydrolyze to the hydroxide. Without separating the iron precipitates, 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 powder as the agent. In the event that all of the cobalt has not been

removed by co-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. Of course, 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.

In carrying the invention into practice, it is preferred to add sulfur dioxide to the purified electrolyte before introduction of the electrolyte into the cathode compartment of the plating operation in such a manner as to ensure substantially uniform distribution of the sulfur dioxide throughout the electrolyte flowing to the cathode cell. Thus, for example, the sulfur dioxide 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 dioxide may likewise be added to the electrolyte in the holding tank. On the other hand, the holding tank may be eliminated and sulfur dioxide may be introduced into the stream of purified electrolyte a suitable distance before the purified electrolyte enters the cathode compartments.

It has been found that the sulfur content of cathode nickel or electronickel produced in accordance with the principles of the present invention has a relation to the concentration of sulfur dioxide present in the electrolyte in the cathode chamber. The following tabulation illustrates that the sulfur content of the resultant electronickel or cathode nickel expressed in percent is substantially equivalent to the concentration of sulfur dioxide (expressed as grams per liter) present in the electrolyte from which said electronickel or cathode nickel was deposited. The electrolyte pH originally was 5.0.

No.	Grams Per Liter SO_2 in Purified Catholyte	pH	Percent Sulfur in Electronickel
1	0.075	4.2	About 0.07 to about 0.08.
2	0.15	3.8	About 0.10 to about 0.15.
3	0.18	3.5	About 0.15 to about 0.20.
4	0.21	3.2	About 0.20 to about 0.22.
5	0.34	2.9	About 0.30 to about 0.35.

Electronickel or cathode nickel produced as described hereinbefore by introducing sulfur dioxide into a nickel plating electrolyte under otherwise normal operating conditions of temperature and current density is satisfactory for use directly, without heat treatment or fusion, as anodes when the sulfur content of the electronickel or cathode nickel is preferably about 0.06% to 0.2%. When the electronickel is corroded in a standard hot Watts bath, the electronickel is active and exhibits good corrosion characteristics throughout the pH range of about 1.5 to 5.5 (Q.), i. e., pH as measured by the standard quinhydrone electrode. In addition, the electronickel corrodes uniformly and does not produce an excessive amount of sludge or loose nickel when corroded as anode in a nickel plating bath.

It has been found that sulfur dioxide is unique for purposes of the invention as compared to inorganic sulfur-containing compounds, such as salts, which might be considered to have analogous properties. Thus, it has been found that

additions of salts, like sulfites, etc., of the alkali and alkaline earth metals, to nickel electrolytes require further modifications of the electrolyte for the purpose of producing sulfur-containing electronickel therefrom. Thus, it has been found necessary to make acid additions in order to control the pH of electrolytes containing such salts before the amounts of sulfur contemplated by the invention can be introduced into the electronickel deposited therefrom. However, unforeseen results have been achieved when additions of sulfur dioxide have been made to a nickel plating electrolyte in accordance with the invention. The sulfur dioxide has been found to perform a very important and unique dual function in the nickel plating bath, i. e., additions of sulfur dioxide provide a source of sulfur for deposition in nickel electrodeposited from said electrolyte and, at the same time, provide the required pH control in said electrolyte which enables deposition of sulfur along with the nickel electrodeposited from the nickel electrolyte to produce sulfur-containing electronickel. When the required pH control has been established by introduction of sulfur dioxide into the electrolyte, it must not be detrimentally affected as by the introduction of subsequent basic additions and the resultant neutralization of the acid. If the pH control is detrimentally affected, sulfur will not be deposited at the cathode along with the electrodeposited nickel as contemplated by the invention when such an electrolyte is used in the production of electronickel.

Electronickel containing sulfur in excess of about 0.06% is somewhat brittle and presents some difficulty in shearing although it is satisfactory for use directly, without fusion, as anode material in the protective and/or decorative electroplating of nickel. 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 electronickel can be overcome. When copper is added to electronickel and correlated to the amount of sulfur present therein, electronickel containing sulfur in excess of about 0.06% can be produced which not only has all the desirable anode corrosion characteristics, but in addition has improved ductility. At least about 0.05% copper should be introduced into the sulfur-containing electronickel of the invention to promote ductility therein. In the presence of such amounts of copper up to about 0.15%, the sulfur content of cathode nickel can be from about 0.06% to as much as 0.15% to provide electronickel which is satisfactory for use as anode without heat treatment and in the unfused condition throughout the pH range of about 1.5 to about 5.5 (Q.), and to provide copper-sulfur-bearing electronickel which has less tendency to brittleness and can be sheared into sizes suitable for use as anode.

The copper-bearing modified electronickel containing sulfur may be produced in a manner quite analogous to that described hereinbefore for the production of modified electronickel 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 purified 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 0.01 to about 0.03 gram per liter of electro-

lyte. The copper compound may be introduced simultaneously with the sulfur dioxide, or at any other suitable time or place which will permit substantially complete mixing of the copper compound with the purified electrolyte before the electrolyte enters the cathode compartment. 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 and copper, or the copper salt or the copper compound may be introduced into a holding tank together with sulfur dioxide as indicated hereinbefore. Alternatively (although less preferably, because of control difficulties), the removal of copper from the impure electrolyte may be regulated to leave in the purified electrolyte a residual amount of copper within the limits set forth hereinbefore. In other respects the production of copper-bearing modified electronickel containing sulfur is carried out under the same conditions as those employed to produce substantially copper-free modified electronickel containing sulfur.

It has been found that the tolerance of electronickel for sulfur can be increased by introducing into the electronickel a controlled amount of carbon with or without the controlled amount of copper and that desirable anode properties including appearance, etc. are improved by such carbon additions as well as the aforedescribed copper additions. That is to say, electronickel containing about 0.02% to 0.04% carbon, about 0.05% to 0.15% copper, and about 0.10% to 0.15% 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 sulfur dioxide. The acetylene is introduced into the electrolyte in amounts sufficient to provide a concentration of about 0.001 to about 0.005 grams of acetylene per liter of electrolyte. Simultaneously, provision is made to provide about 0.01 to about 0.03 gram per liter of copper and about 0.10 to about 0.15 gram of sulfur dioxide per liter of electrolyte. The temperature, current density and pH of the electrolyte during electrodeposition of the carbon-copper-bearing modified electronickel containing sulfur are substantially the same as those set forth hereinbefore for the manufacture of the novel sulfur-bearing electronickel of the invention.

When desired, electronickel containing sulfur and carbon but substantially devoid of copper can be produced by making suitable additions within the ranges set forth hereinbefore of sulfur dioxide and acetylene to the purified electrolyte and maintaining suitable concentrations of sulfur dioxide and acetylene in the purified electrolyte entering the cathode compartment. Thus, when a sulfur dioxide concentration of about 0.06 to about 0.2 gram per liter and an acetylene concentration of about 0.001 to about 0.005 gram per liter is maintained in the purified catholyte, electrolytic nickel containing about 0.06% to about 0.2% sulfur and about 0.01 to about 0.04% carbon can be electrodeposited therefrom under the conditions indicated hereinbefore. It is to be noted that this aspect of the invention advantageously provides a method for manufacturing carbon-sulfur-bearing electronickel wherein only gaseous electrolyte addition agents, easly removable at will from the electrolyte, are employed.

As indicated hereinbefore, particularly desirable anode characteristics are obtained in sulfur-bearing electrolytic nickel or cathode nickel containing about 0.06% to about 0.2% sulfur. Sulfur-carbon-bearing electrolytic nickel or cathode nickel containing about 0.1% to about 0.15% sulfur and about 0.01% to about 0.04% carbon also gives very satisfactory results when used as anode in the decorative and/or protective electroplating of objects with nickel. Similarly, sulfur-carbon-copper-bearing electrolytic nickel or cathode nickel containing about 0.1% to about 0.15% sulfur, about 0.01% to about 0.04% carbon and about 0.05% to about 0.15% copper also gives very satisfactory results. When sulfur-copper-bearing electrolytic nickel is desired, sulfur contents between about 0.1% and about 0.15% together with copper contents between about 0.05% and about 0.15% have been found to be preferable.

As those skilled in the art know, electrolytic nickel is of very high purity and varies but slightly in composition whether produced in an all-sulfate electrolyte, an all-chloride electrolyte, or a mixed sulfate-chloride electrolyte. Electrolytic nickel produced according to the present invention may contain, in addition to the amounts of sulfur and/or copper and/or carbon disclosed hereinbefore, about 0.001% to about 0.005% iron and about 0.01% to 0.8% cobalt.

This application is a continuation-in-part of my co-pending U. S. application Serial No. 497,601, filed August 6, 1943, now Patent No. 2,453,757.

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 and scope of the specification and the appended claims.

I claim:

1. The process of electrorefining impure metallic nickel to produce substantially pure nickel containing copper, carbon and sulfur and having good activity when employed as anode in electroplating nickel from nickel electroplating baths having a pH up to 5.5 (Q.) which comprises anodically corroding an impure nickel anode to produce an impure electrolyte containing the impurities copper, arsenic, iron and lead, purifying said electrolyte to produce a purified electrolyte substantially devoid of copper, arsenic, iron and lead, introducing into said purified electrolyte a sufficient amount of sulfur dioxide to provide a concentration of about 0.1 to 0.15 gram per liter of sulfur dioxide, a sufficient amount of an electrolyte-soluble copper salt to provide a concentration of about 0.01 to 0.03 gram per liter of copper, and a sufficient amount of acetylene to provide a concentration of about 0.001 to 0.005 gram per liter therein, and electrodepositing substantially pure nickel from said electrolyte in the presence of said amounts of sulfur dioxide, copper and acetylene without neutralizing the effects of said sulfur dioxide upon the electrolyte pH while depositing sulfur within the range of about 0.1% to 0.15%, copper within the range of about 0.05% to 0.15% and carbon within the range of about 0.01% to 0.04% in said nickel.

2. The process of electrorefining impure metallic nickel to produce substantially pure nickel containing carbon and sulfur and having good activity when employed as anode in electroplating nickel from nickel electroplating baths having a pH up to 5.5 (Q.) which comprises anodically corroding an impure nickel anode to pro-

duce an impure electrolyte containing the impurities copper, arsenic, iron and lead, purifying said electrolyte to produce a purified electrolyte substantially devoid of copper, arsenic, iron and lead, introducing into said purified electrolyte a sufficient amount of sulfur dioxide to provide a concentration of about 0.1 to 0.15 gram per liter of sulfur dioxide and a sufficient amount of acetylene to provide a concentration of about 0.001 to 0.005 gram per liter therein, and electrodepositing substantially pure nickel from said electrolyte in the presence of said amounts of sulfur dioxide and acetylene without neutralizing the effects of said sulfur dioxide upon the electrolyte pH while depositing sulfur within the range of about 0.1% to 0.15% and carbon within the range of about 0.01% to 0.04% in said nickel.

3. The process of electrorefining impure metallic nickel to produce substantially pure nickel containing copper and sulfur and having good activity when employed as anode in electroplating nickel from nickel electroplating baths having a pH up to 5.5 (Q.) which comprises anodically corroding an impure nickel anode to produce an impure electrolyte containing the impurities copper, arsenic, iron and lead, purifying said electrolyte to produce a purified electrolyte substantially devoid of copper, arsenic, iron and lead, introducing into said purified electrolyte a sufficient amount of sulfur dioxide to provide a concentration of about 0.1 to 0.15 gram per liter of sulfur dioxide and a sufficient amount of an electrolyte-soluble copper salt to provide a concentration of about 0.01 to 0.03 gram per liter of copper, and electrodepositing substantially pure nickel from said electrolyte in the presence of said amounts of sulfur dioxide and copper without neutralizing the effects of said sulfur dioxide upon the electrolyte pH while depositing sulfur within the range of about 0.1% to 0.15% and copper within the range of about 0.05% to 0.15% in said nickel.

4. The process of electrorefining impure metallic nickel to produce substantially pure nickel containing copper and sulfur and having good activity when employed as anode in electroplating nickel from nickel electroplating baths having a pH up to 5.5 (Q.) which comprises anodically corroding an impure nickel anode to produce an impure electrolyte containing the impurities copper, arsenic, iron and lead, purifying said electrolyte to produce a purified electrolyte substantially devoid of copper, arsenic, iron and lead, introducing into said purified electrolyte a sufficient amount of sulfur dioxide to provide a concentration of about 0.06 to 0.15 gram per liter of sulfur dioxide and a sufficient amount of an electrolyte-soluble copper salt to provide a concentration of about 0.01 to 0.03 gram per liter of copper, and electrodepositing substantially pure nickel from said electrolyte in the presence of said amounts of sulfur dioxide and copper without neutralizing the effects of said sulfur dioxide upon the electrolyte pH while depositing sulfur within the range of about 0.06% to 0.15% and copper within the range of about 0.05% to 0.15% in said nickel.

5. The process for producing electrolytic nickel satisfactory for use directly in nickel electroplating baths as a nickel plating anode and having good activity up to about pH 5.5 (Q.) which comprises incorporating sulfur dioxide into a purified nickel refining electrolyte selected from the group consisting of all-sulfate electrolytes, all-chloride electrolytes, and sulfate-chloride electrolytes to provide a concentration of about 0.06 to about 0.2 gram per liter of sulfur dioxide in said electrolyte and to substantially reduce the pH of said electrolyte, the electrolyte pH after said sulfur dioxide introduction being within the range of about 2.0 to about 4.5, and said sulfur dioxide being the sole active agent for introducing sulfur into nickel electrodeposited from said eletcrolyte, electrodepositing substantially pure nickel from said electrolyte in the presence of said sulfur dioxide without neutralizing the effects of said sulfur dioxide in reducing the electrolyte pH while depositing sulfur within the range of about 0.06% to about 0.2% in said nickel to produce electrolytic nickel having good activity when used directly as anode in electrodepositing nickel from nickel electroplating baths, thereafter aerating said electrolyte to provide a purified nickel refining electrolyte substantially devoid of sulfur dioxide and satisfactory for use in electrodepositing electrolytic nickel of high purity substantially devoid of sulfur.

6. The process for producing electrolytic nickel satisfactory for use directly in nickel electroplating baths as a nickel plating anode and having good activity up to about pH 5.5 (Q.) which comprises incorporating sulfur dioxide into a purified nickel refining electrolyte selected from the group consisting of all-sulfate electrolytes, all-chloride electrolytes, and sulfate-chloride electrolytes to provide a concentration of about 0.06 to about 0.5 gram per liter of sulfur dioxide in said electrolyte and to substantially reduce the pH of said electrolyte, the electrolyte pH after said sulfur dioxide introduction being within the range of about 2.0 to about 4.5, and said sulfur dioxide being the sole active agent for introducing sulfur into nickel electrodeposited from said electrolyte, electrodepositing substantially pure nickel from said electrolyte in the presence of said sulfur dioxide without neutralizing the effects of said sulfur dioxide in reducing the electrolyte pH while depositing sulfur within the range of about 0.06% to about 0.5% in said nickel to produce electrolytic nickel having good activity when used directly as anode in electrodepositing nickel from nickel electroplating baths, and thereafter aerating said electrolyte to provide a purified electrolyte substantially devoid of sulfur dioxide and satisfactory for use in electrodepositing nickel of high purity substantially devoid of sulfur.

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