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ANODE PRODUCTION

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This invention relates to anodes, and more particularly to nickel anodes and processes for producing them in which electrolytically deposited nickel is heat-treated and then quenched in sulfuric acid.

When anodes of electrolytic cathode nickel are employed in the usual nickel plating solutions, the rate of corrosion of such anodes is ordinarily slower than the rate at which nickel is removed from the solution, so that the dissolved nickel content of the plating solution becomes depleted. In Hogaboom U. S. Patent 1,433,618 there is described a process for heat-treating such nickel anodes to improve their corrosion in nickel electroplating baths. Following the heat treatment, the nickel is cooled by air cooling or quenching.

Unfortunately, quenching of heated nickel in the usual media or by air cooling results in the formation of a passive nickel oxide on the surface of the nickel, and this nickel oxide coating is exceptionally resistant to attack upon being made anodic in the usual nickel plating solutions. The oxide film must therefore be removed, and this is done by procedures commonly known as "deskinning." Such "deskinning" operations, being an extra step in the manufacture of nickel anodes, add appreciably to the cost of the anodes, besides being wasteful of the nickel.

The media heretofore available for quenching nickel have, moreover, not been entirely suitable on account of certain of their physical and chemical properties. Thus, when water is the medium used for quenching, a portion of the water coming into immediate contact with the nickel is converted to steam, and this steam insulates the nickel momentarily against further contact with the water, and thereby retards the rate of heat transfer to the water. This insulating action is not uniform; hence, the grain structure of the quenched anode becomes irregular. If oil is used as a quenching medium, the heat treated anodes must first be cooled below the ignition temperature of the oil, as for instance by air cooling, and the relatively slow rate at which such preliminary cooling occurs tends to permit resumption of the crystal structure which the nickel had before the heat treatment. Moreover, the oil must be removed from the quenched anodes before they are used in nickel plating solutions, and such removal entails still another step in the operation. Other quenching media heretofore used suffer from disadvantages similar to those just described for water or for oil.

Now I have found that nickel anodes having improved corrosion characteristics in electroplating solutions may be produced by heat-treating electrolytic cathode nickel and then quenching the nickel in a medium comprising concentrated sulfuric acid. Anodes so produced require no deskinning treatment to make them suitable for use. Moreover, they have a uniform and large grain structure and are characterized by even, rapid corrosion during use in nickel plating solutions.

The nickel which may be treated according to the processes of my invention preferably may be in the physical form in which it customarily occurs when produced as a cathodic deposit from electrolytic refining baths, running up to one-half inch or more in thickness. It may be suitably supported as, for instance, on a sheet of nickel supported on a strap for making contact with a source of electric current and for suspending the nickel in the plating solution, or it may be supported directly on such a strap. Alternatively, the nickel may be in the form of cast electrodes prepared by melting cathode nickel and casting it to any desired shape, but such casting entails an extra operation and ordinarily there is no advantage to be gained therefrom.

If desired, there may be included in the cathode nickel small amounts of other metals such as cobalt, cadmium or zinc. The amount of such additional metals used will ordinarily be relatively small, for instance, less than about one per cent.

To heat treat nickel preparatory to quenching it in sulfuric acid according to a process of my invention, the nickel is heated by suitable means to a temperature at which crystal transformation will occur. A temperature in the range from about 500 to about 1000° C. is ordinarily suitable, a temperature of about 800° C. being usually preferred. The rate of heating and the time at which the maximum temperature is maintained should be sufficient to permit crystal transformation and will depend upon such factors as the thickness of the nickel and the temperature attained. Once the nickel has been heated through, a few minutes will ordinarily suffice to permit crystal transformation.

To quench heated nickel for anodes in accordance with a process of my invention, the nickel is introduced into a body of concentrated sulfuric acid. Preferably the body of sulfuric acid is contained in a tank or other suitable receptacle of such size that the nickel may be completely submerged in the acid. It is desirable that the amount of acid be relatively large as compared with the amount of nickel in order that quench-

ing may be rapid and that the temperature of the acid will not be raised to an excessive degree. It will be apparent that discretion should be exercised in introducing the heated nickel into the acid to avoid raising the temperature of the acid suddenly above its boiling point. The conditions within the sulfuric acid quenching bath should be such as will cool the nickel rapidly to a temperature below its critical range, that is, a temperature below that at which crystal transformation occurs.

For best results the sulfuric acid used for quenching should be relatively concentrated. Ordinarily it is preferable that the quenching bath contain no less than about seventy-three per cent by weight of H_2SO_4, while an acid containing from about ninety-two to about one hundred per cent by weight of H_2SO_4 is even more to be preferred. As compared with other quenching media, sulfuric acid in these concentrations has a relatively high heat capacity and hence is particularly well adapted for the purpose.

The temperature of the acid used should preferably be held at a point substantially below its boiling point. This may be done by using large amounts of acid relative to the amount of nickel quenched, or by cooling the acid by a suitable means such as cooling coils. Means for circulating the acid in contact with the nickel to be cooled may also be provided so as to obtain uniformity of temperature throughout the body of acid used.

In combination with the sulfuric acid employed, there may also be used other acids such as hydrochloric acid to improve further the corrodibility of the quenched nickel in nickel plating baths.

The anodes produced by heat treating nickel and quenching it in sulfuric acid in accordance with a process of my invention are characterized by ready solubility when made anodic in nickel plating baths and particularly in such baths as those containing nickel sulfate in which dissolution of nickel anodes has heretofore been a problem. The anodes are further characterized by a uniform and relatively large crystal grain structure. The uniformity of grain structure causes the anodes to corrode evenly when used in nickel plating baths, and such evenness of corrosion permits an increased proportion of the nickel present to serve its intended purpose of supplying nickel to the plating bath, there being a corresponding decrease in the amount of nickel lost due to sludge formation and corroding off of the anodes.

Nickel anodes produced according to the processes of my invention are further characterized by their freedom of a surface coating of oxide and by the fact that their nickel content is the same as the untreated anode from which they were produced, since the freedom from surface oxide makes deskinning unnecessary. The surfaces of the anodes are relatively smooth as compared with deskinned anodes because of the avoidance of a deskinning operation.

The foregoing description of my invention is further illustrated in the following examples:

Example I

Anodes fashioned from commercial electrolytically produced cathode nickel were heated to 800° C. for 30 minutes in a muffle furnace. The anodes were then immediately submerged completely in commercial concentrated sulfuric acid containing ninety-six per cent by weight of H_2SO_4. When the anodes had cooled to approximately 50° C., they were removed from the acid, washed, and introduced as anodes in a Watts nickel-plating solution having the following approximate composition:

	Oz./gal. solution
Nickel sulfate, $NiSO_4 \cdot 7H_2O$	32
Nickel chloride, $NiCl_2 \cdot 6H_2O$	6
Boric acid, H_3BO_3	4

The solution was then worked for an extended period at 120° F. and a current density of 35 amperes per sq. ft. of cathode, after which its nickel content was determined analytically. The nickel content was found to be substantially the same as at the start of the period of use, indicating that the nickel of the sulfuric acid-quenched anode dissolved at a rate sufficiently rapid to avoid depletion of the nickel content of the bath. Examination of the anode showed that it had corroded evenly and that its surface was relatively smooth, the amount of sludge formation and metal loss due to uneven corrosion being relatively small as compared with the usual amount of sludge formation and metal loss occurring under similar conditions with anodes heat treated by processes heretofore used.

Example II

Anodes prepared by electrolytically depositing nickel upon a sheet of pure nickel suitably supported by straps to a total thickness of one-half inch were heated to 800° C. for thirty minutes in a muffle furnace. The anodes were then immediately submerged completely in a medium comprising ten per cent by volume of commercial 20° Bé. muriatic acid and ninety per cent by volume of sulfuric acid containing ninety-six per cent by weight H_2SO_4. When the anodes had cooled to approximately 100° C. they were removed from the acid, washed and further cooled with water and introduced as anodes in a Watts nickel plating solution having approximately the composition shown in Example I. The solution was then used for an extended period for depositing nickel upon a cathode, a temperature of 120° F. and a current density of 35 amperes per square foot of cathode being maintained. By analytical methods the nickel contents of the bath were both found to rise slowly during use.

It will be observed that the rate of corrosion of the anode prepared according to Example II was such as to permit an increase in the nickel content of the plating solution in which the anodes were used. This is, of course, a desirable characteristic since such an increase will offset nickel losses due to dragout when such nickel plating solutions are used in commercial operations.

While I have shown certain illustrative anodes and processs, it will be understood that one skilled in the art may without departing from the spirit of this invention devise numerous processes and produce numerous anodes.

I claim:

1. In a process for producing from nickel, the steps comprising heating the nickel to a temperature above its critical temperature, and quenching it in concentrated sulfuric acid.

2. In a process for producing anodes from nickel, the steps comprising heating the nickel to a temperature in the range from about 500 to 1000° C., and then quenching it in concentrated sulfuric acid to a temperature below its critical temperature.

3. In a process for producing anodes from nickel, the steps comprising heating the nickel to about 800° C., and then quenching it to a temperature below its critical temperature in a sulfuric acid solution containing not substantially less than about seventy-three per cent H_2SO_4.

4. In a process for producing anodes from electrolytically deposited cathode nickel, the steps comprising heating the nickel to about 800° C., and then immediately quenching it to a temperature below its critical temperature range by immersing it completely in a bath containing about ninety-six per cent by weight of H_2SO_4.

5. In a process for producing anodes from electrolytically deposited cathode nickel, the steps comprising heating the nickel to about 800° C., and then immediately quenching it to a temperature below its critical temperature range by immersing it completely in a bath comprising about ten per cent by volume of 20° Bé. muriatic acid solution and ninety per cent by volume of concentrated sulfuric acid containing about ninety-six per cent by weight of H_2SO_4.

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