March 25, 1930. W. J. HARSHAW ET AL 1,751,630

ANODE AND METHOD OF MAKING SAME

Filed Nov. 28, 1927

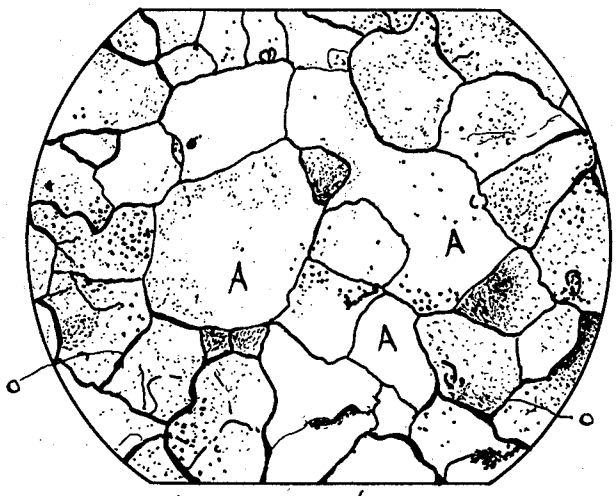


Fig. 1.

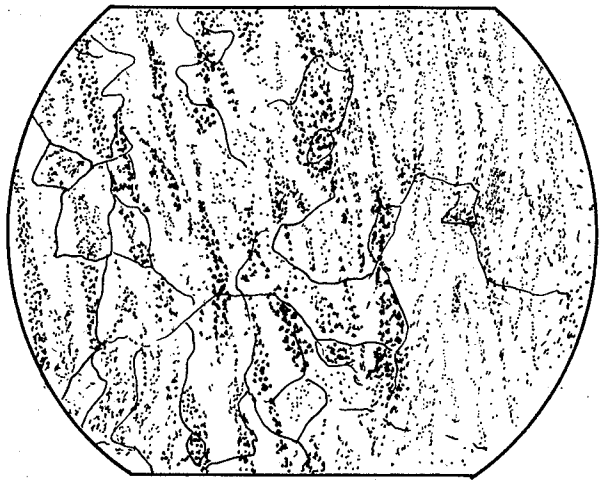


Fig. 2

INVENTORS
William J. Harshaw,
Paul M. Savage and
BY Fred K. Bezzenberger.
Fay Oberlin & Fay
ATTORNEYS.

Patented Mar. 25, 1930 1,751,630

UNITED STATES PATENT OFFICE

WILLIAM J. HARSHAW, OF SHAKER HEIGHTS, PAUL M. SAVAGE, OF ELYRIA, AND FRED K. BEZZENBERGER, OF CLEVELAND HEIGHTS, OHIO, ASSIGNORS, BY MESNE ASSIGNMENTS, TO THE INTERNATIONAL NICKEL COMPANY, INC., OF NEW YORK, N. Y., A CORPORATION OF DELAWARE

ANODE AND METHOD OF MAKING SAME

Application filed November 28, 1927. Serial No. 236,123.

The customary nickel anodes as used in electro-deposition tend to corrode unevenly and to present areas of passive surface, while also separating off sludge particles into the bath, portions tending to adhere to and roughen the surface of the work; and such disadvantages become more prominent when considerable current density is employed as in accordance with the tendencies of recent practice. As a further result, the bath shows premature impoverishment due to the failure of the anode to dissolve as fast as the metal deposits on the cathode, although a considerable waste of metal occurs in sludge. The avoidance of these difficulties is of fundamental importance and more satisfactory anodes are highly desirable. Various attempted remedies have been suggested along lines of specially purified metal. Also special compositions, including oxygen-containing nickel, have been proposed, but the problem remained. In accordance with our present invention however, anodes may be had affording efficiently active surfaces capable of corroding uniformly and without detrimental waste.

To the accomplishment of the foregoing and related ends, the invention, then, consists of the features hereinafter fully described, and particularly pointed out in the claims, the following description setting forth in detail certain features embodying the invention, such being illustrative however of but a few of the various ways in which the principle of the invention may be employed.

In said annexed drawing:—

Fig. 1 represents a microscopic view of the metallic structure at the initial stage of manufacture in accordance with our invention; and Fig. 2 is a similar view of the structure as completed.

In its general aspects, our invention contemplates providing what we may designate as passivity-inhibiting material in the metal and homogenizing the mass into an intimate substantially uniform distribution through the metal.

As such passivity-inhibiting material, we employ agents having a relative electro-chemical relation to the metal, for example preferably oxides, as of nickel, cobalt, copper, etc., these being at present the most advantageous of the agents readily available, and oxygen particularly may be cheaply introduced into the metal while molten. When the metal containing such material is cast, and is examined microscopically, it presents a markedly granular structure with the metal crystals some quite wholly free from any content of the added material and some containing it, but the material is especially massed at the grain boundaries. A microscopic section from a cast ingot of nickel for instance containing oxygen as a nickel-nickel oxide eutectic (as we may designate it) shows a structure as in the sample represented in Fig. 1. The crystals of nickel A are seen to be distinctly separated and presenting the aspect of distinct grains or crystals with well defined boundaries in which granules are massed; that is the metal crystals are separated by segregated nickel oxide *o*. Some of the metal crystals are substantially clear of oxide content, while some show its presence. The metal at this stage is thus heterogeneous in two senses, the eutectic distribution involving a predominance of oxide especially at the grain boundaries, and to such extent as there may be some inclusions within the grain, some of the grains contain it and others do not.

It has been generally held in the art that nickel with such content as oxide could not be modified in its properties, or be mechanically worked because of its pronounced brittleness. We have now found however, that by suitable procedure, such material may be mechanically worked, on being heated to a temperature of sufficient degree, and it may be plastically deformed without fracture or incipient fracture.

As an illustration of our process, metal for the anode, nickel containing a small per cent of oxygen, for example .05–.25%, and preferably substantially sulphur free, is heated to a temperature desirable, for instance about 1700 to 2400° F. and is subjected to mechanical working, as rolling, hammering and forging, or swaging, etc. The hammering or equivalent plastic deformation should be dis-

continued before the metal cools materially. The metal may be reheated and worked to a further extent, as may be desired. If working be stopped at a temperature above annealing temperature of the nickel, naturally the product will be annealed.

In such working, we may reduce the metal to a greater or less extent as regards its mechanical form compared with the original ingot, and we have found in general that a sectional reduction of at least 3 to 1 is desirable, and further advantage may be had by working out an ingot to a reduction ratio of even higher order, for instance as high as 60 to 1. On being brought to incipient plasticity, and subjected to mechanical deformation, there is brought about progressively an obliteration of the old grain boundaries, and at such temperature recrystallization will go forward and new grain boundaries are formed and additionally there is a homogenizing of the eutectic into the various grains. A mass of nickel thus initially containing a small per cent of oxygen as nickel-nickel oxide eutectic may be homogenized into inter and intra granular uniformity such as to evenly and uniformly distribute the compounds throughout the mass, the grain boundaries which were present in the original cast metal having been obliterated by the plastic deformation in the working, with substantially simultaneous regeneration into new grain boundaries, which have a content of oxygen or other passivity-inhibiting material substantially identical with that within the grains. There is thus presented a mass which is of practically homogeneous character as regards distribution of the nickel-nickel oxide eutectic, rather than segregation between boundaries of nickel grains, such nickel crystals containing a larger percentage of eutectic material than is normally present therein as cast. Moreover, the original non-uniform distribution of the oxide, some grains having a content and some having none, is replaced by a fine homogeneous structure, the originally distinctive boundaries of oxide segregation being finally brought into the condition in which the mass is intermingled and amalgamated in admixture, with a substantially uniform distribution of the eutectic. As shown in Fig. 2, a microscopic section of equal magnification as that of Fig. 1 presents as a finished material the aspect of nickel-nickel oxide mass with relatively even distribution and homogeneity throughout.

As a result of our process, anodes are had which when subjected to the corrosion conditions of an electro-deposition bath afford uniformly smooth clear metallic surfaces, with substantial absence of tendency to form passive films with subjacent nickel oxide. Moreover the rate of corrosion from the anode surface is such as to satisfy the requirements of the bath without impoverishment thereof and the rate of operation may be maintained at a highly satisfactory level. By reason of the absence of a special sludge formation and separation of floating particles from the anode, the surface of the work remains clear and smooth and is readily finally buffed into a highly satisfactory finish. It is to be noticed furthermore that an anode as produced in accordance with our process shows a material densifying of the metal, in distinction to the porous more or less open texture. In the claims hereinafter, in employing for conciseness the term "nickel-nickel oxide eutectic", we refer to such condition substantially as shown in our illustration.

Other modes of applying the principle of the invention may be employed, change being made as regards the details disclosed, provided the means stated in any of the following claims, or the equivalent of such, be employed.

We therefore particularly point out and distinctly claim as our invention:—

1. An anode for electro-deposition, comprising nickel containing from 0.05 to 0.25 per cent of oxygen as nickel-nickel oxide eutectic, and being of substantially uniform composition within and without its grain structure.

2. A rolled nickel anode containing substantially 0.24 per cent of oxygen.

3. A rolled nickel anode substantially free from impurities and containing substantially 0.24 per cent of oxygen.

4. An anode for electro-deposition, comprising nickel containing 0.05 to 0.25 per cent of oxygen-containing eutectic substantially uniformly intermingled within the nickel crystals.

5. An anode for electro-deposition, including rolled nickel containing 0.05 per cent of oxygen as nickel-nickel oxide eutectic.

6. A method of making anodes, which comprises heating nickel containing nickel-nickel oxide eutectic to a workable plasticity, and rolling while at such workable temperature.

7. A method of making anodes, which comprises heating nickel containing .05–.25% of oxygen as nickel-nickel oxide eutectic to a workable plasticity, and working the metal.

8. A method of making anodes, including heating nickel containing .05–.25% of oxygen to a temperature of about 1800 to 2400° F. and working the metal to distribute the eutectic substantially uniformly throughout the anode material.

Signed by us this 25th day of November, 1927.

WILLIAM J. HARSHAW.
PAUL M. SAVAGE.
FRED K. BEZZENBERGER.