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ELECTRODEPOSITED ARTICLE AND METHOD OF MAKING THE SAME

Original Filed Aug. 15, 1919

Fig. 1

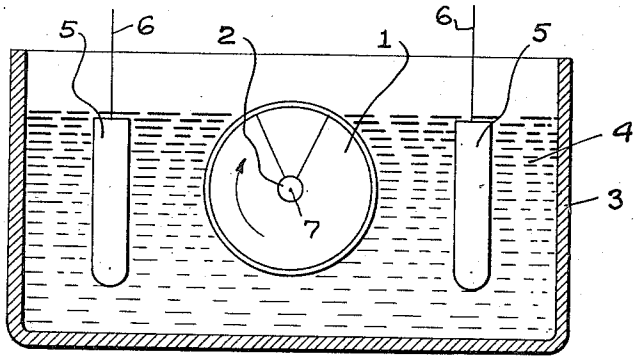
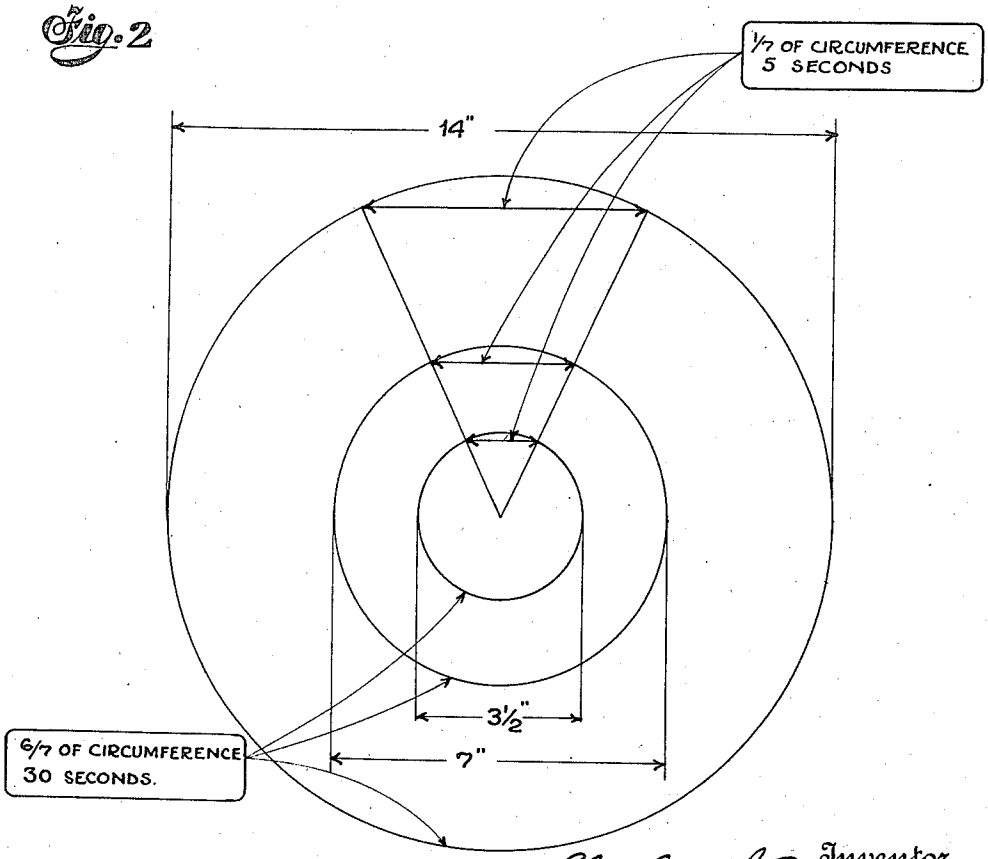


Fig. 2



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UNITED STATES PATENT OFFICE.

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ELECTRODEPOSITED ARTICLE AND METHOD OF MAKING THE SAME.

Application filed August 15, 1919, Serial No. 317,656. Renewed January 21, 1924.

To all whom it may concern.

Be it known that I, CHARLES P. MADSEN, a citizen of the United States, and a resident of the city, county, and State of New York, have invented an Improvement in Electrodeposited Articles and Methods of Making the Same, of which the following is a specification.

My invention relates to methods of electrodepositing metals, particularly the "nickel-metals," by which I mean nickel, or cobalt, or alloys containing substantial amounts of nickel, or of cobalt, or of both of these metals, the invention comprising also articles made of such "nickel-metals" by electrodeposition. The present invention aims to provide improved methods of electrodepositing metals, especially the "nickel-metals" referred to above, particularly, but not exclusively, in tubular form, and aims also to provide articles, particularly of tubular form, made of such "nickel-metals" by electrodeposition.

By way of example I shall describe herein illustrative embodiments of the methods and of the articles of my invention. In practicing the method comprising one such illustrative embodiment, I may employ the apparatus diagrammatically illustrated in: Figure 1 of the accompanying drawings; Figure 2 being a diagram illustrating certain time and space relationships which may be utilized in practicing said illustrative embodiment of the method.

I shall describe the method comprising such illustrative embodiment in connection with the bath and the new nickel described in my copending application, Serial No. 292,794 filed April 26, 1919. In practicing said method, I may employ a substantially circular cylindrical cathode 1 mounted for rotation on a shaft 2 which may be rotated by any suitable means, not shown.

The cathode may be made of an easily fusible metal, cast about the shaft, if a separable deposit, such as a nickel tube, is desired. In such a case the fusible metal core may readily be melted out when the deposit has reached the desired thickness. If an adherent deposit, such as a nickel coating, is desired, the object to be coated is suitably supported on the shaft 2. The shaft itself may be supported in stuffing boxes, not shown, placed in the sides of the vat or tank 3 containing the bath 4. 5, 5 are the anodes which, in the example here given, may consist of cast nickel. Contact may be maintained with the anodes, by means of the leads 6, 6, attached thereto, and with the cathode by means of the lead 7 through the shaft 2.

In practicing the hereindescribed illustrative embodiment of the method of my invention, I may use an electrodeposition bath of approximately the following composition:

Nickel sulphate, 240 g.
Nickel chloride, 20 g.
Boric acid, 40 g.
Water, 1 liter.

This bath is preferably operated at a temperature of about 130° F. Except for the addition of boric acid, as set forth above, the bath should be neutral.

In order that the electrodeposited metal, such as the nickel, in the example given, may not only be dense, reguline and substantially free from pores and hydrogen, but in order also that said metal shall be free from what are known as "pits" in the art of the deposition of the "nickel metals," I add to the bath, preferably before starting the electrodeposition, a quantity of finely divided nickel hydrate. Preferably I employ freshly precipitated nickel hydrate (NiO_2H_2), probably existing in a colloidal condition, which nickel hydrate remains in suspension in the bath during electrodeposition. While the quantity of hydrate so added may vary within considerable limits, I prefer to add from about 1 to about 5 grams, generally about 1 gram, of said colloidal nickel hydrate to each liter of bath solution.

This colloidal nickel hydrate may be prepared in any suitable manner, as well known to those skilled in the art, for example, by adding an aqueous solution of caustic soda to an excess of an aqueous solution of nickel sulphate, and after decanting the supernatant liquid adding the colloidal nickel hydrate thus produced, with or without washing, to the electrolyte.

I find that by adding to the bath certain salts, such as the sulphates, of the alkali metals, preferably sodium, finely divided or colloidal nickel hydrate is produced and held in suspension in the bath during deposition. This freshly and continuously produced hydrate replenishes the initially

added or subsequently generated nickel hydrate which, during the operation of the bath, aggregates or for other reasons goes out of suspension and drops to the bottom of the bath. Such salts have further beneficial effects and markedly improve the operation of the bath and the character of the deposits formed. For this purpose I may add varying amounts, such as from about 1 to about 10 grams, preferably about 1 gram, of sodium sulphate for each liter of bath solution.

The action of the colloid-producing substances, such as the sodium sulphate, described above, is probably to produce by and during electrodeposition some caustic soda or sodium hydroxide. The caustic soda or sodium hydroxide thus produced, by interaction with the nickel salts present in the bath, such as the nickel sulphate, generates finely divided or colloidal nickel hydrate which remains suspended in the bath. The interaction at the same time re-generates the sodium sulphate.

The rotating cathode on which the deposit takes place has a portion thereof extending out of the bath into a gaseous medium, preferably of an oxidizing nature, such as the air. The angular velocity of rotation of the cathode and the portion of the same exposed to the surrounding air should be so chosen that the time during which the cathode and any portion of the electrodeposited metal carried by it are exposed to the air should be more than what I term the "minimum" or "hydrogen dissipation" period, in order to permit the hydrogen deposited with the metal to be dissipated or removed by contact with the surrounding gaseous medium. This "minimum" or "hydrogen dissipation" period may readily be determined by trial and experiment, and is generally greater than about one-half of a second, usually from one to two seconds.

The time during which the cathode and any portion of the deposit carried by it are exposed to the air should not, however, exceed what I term the "maximum" or "critical" or "separable deposit" period, which, in the case of nickel, is from about 6 to about 16 seconds. By this I mean that if the deposit is exposed to the air longer than said period, on restoring the cathode and its deposit to the bath, the succeeding deposit will not be adherent but will separate or be easily separable from the previous deposit. This results in a laminated, weak, metal, a condition which is obviously to be avoided where a sound, unitary metal is desired.

The "minimum" and "maximum" exposure periods are very little, if at all, affected by the variables of electrodeposition determining the rate of hydrogen formation, the "minimum" exposure period probably depending upon surface phenomena such as the surface tension and the "maximum" exposure period probably being a physical constant of the particular metal being deposited. On the other hand the period of time during which deposition may take place continuously on any portion of the cathode surface between two successive exposures of said surface, which period may be termed the "period of deposition," depends on the factors which determine the rate of formation of hydrogen during deposition. These factors, which include the degree of exactness of neutrality of the bath and the current density employed, may be varied within rather wide limits. By varying these factors the deposition period, and consequently the period of rotation, may be varied through a considerable range. In the case of nickel deposition, using the bath mentioned by way of example herein, the period of rotation may be varied from about 30 seconds to about 10 minutes.

Such a deposition period should be chosen, dependent upon the variable conditions determining the rate of hydrogen formation, that the hydrogen generated will be removed by exposing the cathode before a sufficient quantity has gathered on any portion of its surface and before the hydrogen has remained in contact with any portion of the cathode surface long enough to deleteriously affect the quality of the deposited metal. It may here be stated that it is desirable that the "deposition" period and, consequently, the period of rotation of the cathode be kept as long as is consistent with the various factors referred to, not only to prevent carrying over too heavy a film of electrolyte, as subsequently set forth, but also because it is found that deposition takes place more efficiently at lower speeds of rotation.

All other conditions being fixed, the cathode should rotate once in a period of time equal to the sum of the "exposure" and "deposition" periods, the "exposure" period being, as already stated, probably a physical constant of the metal, and the "deposition" period being a function of the variables of deposition determining the rate of hydrogen formation. For a given metal and for a given bath operating under given conditions, the cathode will, therefore, rotate once during a substantially constant period, no matter what its diameter and, therefore, its peripheral speed may be.

There is, however, an upper limit to the angular velocity and, therefore, to the peripheral speed of the rotating cathode, because if such angular velocity and peripheral speed are too high, too great a layer of electrolyte will be carried over by the cathode onto the exposed portion of the same, with a consequent prevention, in part at least, of the proper escape of the hydrogen from the deposit. In such a case the factors

determining the rate of hydrogen formation should be varied so as to reduce such rate to a point such that the rate of rotation of the cathode may be correspondingly reduced below the upper limit referred to. I find that the bath herein mentioned by way of example and kept almost absolutely neutral, and operating at a temperature of 130° F. with a current density of 200 amperes per square foot, the rate of rotation desirable is once in about 5 to 10 minutes, while if the bath is slightly acid the desirable rate of rotation is once in about 1 to 2 minutes.

It will be apparent from the foregoing discussion that the ratio of "exposure" and "deposition" periods determines the ratio of the exposed and submerged portions of the cathode. It will also be apparent from the foregoing discussion that with a given metal and with a given bath operated under given conditions, this ratio of exposed and submerged or unexposed portions of the cathode surface will be constant, no matter what the diameter of the cathode may be, the rate of rotation of the cathode also being constant under such given conditions, while the peripheral speed will of course vary within very wide limits dependent on the diameter of the cathode.

To more specifically illustrate the time and space relationships previously discussed, as applied to the hereindescribed illustrative embodiment of my invention, I shall choose five (5) seconds (which is more than the usual "minimum" and less than the usual "maximum" periods) as the "exposure" period or time during which any part of the electrodeposited surface may be exposed to the air at any one time. I shall choose thirty (30) seconds as the "deposition" period or the time during which the cathode may remain within the bath between successive exposures. This will give thirty (30) plus five (5) or thirty five (35) seconds as the time of one complete rotation of the cathode, which is within the range of the usual periods of rotation. The ratio of 5 to 35 is 1 to 7, and of 30 to 35 is 6 to 7, so that one-seventh part of the cathode surface will be exposed to the air, and six-sevenths of said surface will be immersed in the bath. This relation is diagrammatically illustrated in Figure 2. Assuming, by way of example, that the average outside diameter for the cathode surface is seven (7) inches, this diameter will correspond to a circumference of about twenty-two (22) inches, and with the cathode rotating once every thirty five (35) seconds, this will correspond to a peripheral velocity of the cathode surface of about thirty eight (38) inches, or about three (3) feet, per minute. Other factors being the same, the peripheral velocity, which is in itself not of controlling importance in connection with the present invention, will be proportional to the diameter of the rotating cathode, that is, it will be twice three (3), or about six (6) feet per minute for a cathode fourteen (14) inches in diameter and one half of three (3) or about one and a half ($1\frac{1}{2}$) feet per minute for a cathode three and one half ($3\frac{1}{2}$) inches in diameter, in the example here given.

In certain cases I find that better results are obtainable if the cathode is rotated intermittently, instead of continuously, still having regard for the various time and space factors referred to in connection with the above described embodiment. That is, instead of rotating the cathode at a uniform rate, the cathode may be rotated intermittently so as to expose successive fractions of the same to the air for the desired period, while permitting the cathode to remain stationary between the successive intermittent rotations. I have discovered that this mode of operation produces very satisfactory results in some instances.

In coating hollow cylindrical or other objects on the inside, in those cases where it is either not desirable to prepare a bath of sufficient volume to contain such objects, the electro-deposition may be carried out by passing the current through a bath solution contained entirely within the hollow object. If the object is open at one or both ends, as where it is a pipe intended to be coated on the inside, either or both ends may be closed by means of plugs. An anode, in the form of a rod, may be passed through the plugs and the bath solution may be connected with a reservoir containing further quantities of electrolyte by means of a plurality of tubes also passing through the plugs. The deposition may be carried out by only partially filling the tube with solution and then rotating the same about a substantially horizontal axis, observing time and space relationships analogous to those that have already been set forth in connection with the embodiment first described above. The provision of the reservoir enables the electrolyte to be circulated through the tube whose interior is being coated, thereby constantly providing fresh electrolyte of proper strength.

The resulting product, in the illustrative embodiment first set forth above, comprises an unworked, seamless, electrodeposited nickel tube, the metal of which is dense, reguline, homogeneous, malleable and ductile.

The nickel of which this tube is made is to be differentiated from the usual electrodeposited nickle in that it is substantially free from pores, pits and hydrogen, and is malleable and ductile to a very high degree, unlike the usual electrodeposited

nickel which is pitted and porous, has a large hydrogen content, and is brittle and unworkable.

The nickel herein described differs in character from the nickel obtained by the usual metallurgical processes in that my new nickel is free from the usual "poisons" such as sulphur, silicon, arsenic, carbon, carbides, oxygen and other gases, and oxide-containing compounds, generally present in metallurgical nickel, and rendering the same imperfect and difficult to work.

My new nickel is to be further differentiated from the ordinary metallurgical nickel in that it has a finer and more even grain than such metallurgical nickel. It is also considerably purer than such metallurgical nickel, resists chemical action better, and has a higher melting point.

A further difference in character between my new nickel and the ordinary metallurgical nickel is shown by the fact that the film of oxide formed by heating my new nickel in an oxidizing atmosphere is thinner, finer in texture, and more adherent and flexible than the oxide coating formed by similar treatment of ordinary metallurgical nickel. Furthermore, such oxide coating in the case of my new nickel is of a different color, generally yellow to brown, while the oxide coating on the metallurgical nickel is generally violet or indigo in color.

Where a deposit of cobalt is desired, a cobalt anode is used in place of the nickel anode, and cobalt compounds are used in place of the corresponding nickel compounds. Where alloys of either nickel, or of cobalt, or of both of these metals, are desired, means analogous to the means herein set forth for the deposition of nickel and of cobalt in the desired condition and having the desired properties may be employed.

It is of course, to be understood that the invention is not to be limited to the specific illustrative embodiments thereof, herein described for purposes of illustration only. It is also to be understood that the applicant does not wish to have the invention or the appended claims in any way limited by any particular theory of operation which he may now hold or which may be suggested by the foregoing detailed description.

What I claim is: :

1. A method of electrodepositing metals which comprises rotating the cathode at such an angular velocity and with such a portion of the same exposed to a gaseous medium that successive portions of the electrodeposited metal will be exposed to said medium more than a predetermined "minimum" period, so as to permit the hydrogen in the deposited metal to be dissipated.

2. A method of electrodepositing metals which comprises rotating the cathode at such an angular velocity and with such a portion of the same exposed to a gaseous medium that successive portions of the electrodeposited metal will be exposed to said medium more than a predetermined "minimum" period, so as to permit the hydrogen in the deposited metal to be dissipated, but less than a predetermined "maximum" period, so as to prevent the successive deposits from being separable.

3. A method of electrodepositing "nickel metals" which comprises rotating the cathode at such an angular velocity and with such a portion of the same exposed to a gaseous medium that successive portions of the electrodeposited metal will be exposed to said medium more than a predetermined "minimum" period, so as to permit the hydrogen in the deposited metal to be dissipated.

4. A method of electrodepositing "nickel metals" which comprises rotating the cathode at such an angular velocity and with such a portion of the same exposed to a gaseous medium that successive portions of the electrodeposited metal will be exposed to said medium more than a predetermined "minimum" period, so as to permit the hydrogen in the deposited metal to be dissipated, but less than a predetermined "maximum" period, so as to prevent the successive deposits from being separable.

5. A method of electrodepositing nickel which comprises rotating the cathode at such an angular velocity and with such a portion of the same exposed to a gaseous medium that successive portions of the electrodeposited nickel will be exposed to said medium more than a predetermined "minimum" period, so as to permit the hydrogen in the deposited nickel to be dissipated.

6. A method of electrodepositing nickel which comprises rotating the cathode at such an angular velocity and with such a portion of the same exposed to a gaseous medium that successive portions of the electrodeposited nickel will be exposed to said medium more than a predetermined "minimum" period, so as to permit the hydrogen in the deposited nickel to be dissipated, but less than a predetermined "maximum" period, so as to prevent the successive deposits from being separable.

7. A method of electrodepositing metals which comprises rotating the cathode at such an angular velocity and with such a portion of the same exposed to a gaseous medium that successive portions of the electrodeposited metal will be exposed to said medium less than a predetermined "maximum" period, so as to prevent the successive deposits from being separable.

8. A method of electrodepositing metals which comprises rotating the cathode at such an angular velocity and with such a portion of the same exposed to the air that

successive portions of the electrodeposited metal will be exposed to the air more than a predetermined "minimum" period, so as to permit the hydrogen in the deposited metal to be dissipated, the angular velocity of rotation of the cathode not being sufficiently great to prevent the film of bath liquid initially carried by the successive exposed portions of the rotating cathode from freely flowing off from such portions during the successive exposure periods.

9. A method of electrodepositing metals which comprises rotating the cathode at such an angular velocity and with such a portion of the same exposed to the air that successive portions of the electrodeposited metal will be exposed to the air more than a predetermined "minimum" period, so as to permit the hydrogen in the deposited metal to be dissipated, but less than a predetermined "maximum" period, so as to prevent the successive deposits from being separable, the angular velocity of rotation of the cathode not being sufficiently great to prevent the film of bath liquid initially carried by the successive exposed portions of the rotating cathode from freely flowing off from such portions during the successive exposure periods.

10. A method of electrodepositing "nickel metals" which comprises rotating the cathode at such an angular velocity and with such a portion of the same exposed to the air that successive portions of the electrodeposited metal will be exposed to the air more than a predetermined "minimum" period, so as to permit the hydrogen in the deposited metal to be dissipated, the angular velocity of rotation of the cathode not being sufficiently great to prevent the film of bath liquid initially carried by the successive exposed portions of the rotating cathode from freely flowing off from such portions during the successive exposure periods.

11. A method of electrodepositing "nickel metals" which comprises rotating the cathode at such an angular velocity and with such a portion of the same exposed to the air that successive portions of the electrodeposited metal will be exposed to the air more than a predetermined "minimum" period, so as to permit the hydrogen in the deposited metal to be dissipated, but less than a predetermined "maximum" period, so as to prevent the successive deposits from being separable, the angular velocity of rotation of the cathode not being sufficiently great to prevent the film of bath liquid initially carried by the successive exposed portions of the rotating cathode from freely flowing off from such portions during the successive exposure periods.

12. As an article of manufacture, a seamless electrodeposited tube of unworked, dense, malleable "nickel-metal," substantially free from pores, pits and hydrogen.

13. As an article of manufacture, a seamless electrodeposited tube of unworked, dense, malleable nickel, substantially free from pores, pits and hydrogen.

14. A method of electrodepositing metals on a rotating cathode which comprises maintaining a predetermined portion of the cathode surface exposed to a gaseous medium, the ratio of the exposed to the unexposed portions of the cathode surface being substantially equal to the ratio between the "exposure" period for the particular metal being deposited and the "deposition" period for the particular bath used under the particular conditions employed.

15. A method of electrodepositing metals which comprises rotating the cathode at such an angular velocity and with such a portion of the same exposed to a gaseous medium that successive portions of the electrodeposited metal will be exposed to said medium more than a predetermined "minimum" period, so as to permit the hydrogen in the deposited metal to be dissipated, the "deposition" period being less than a period which, under the particular conditions involved in the deposition would prevent the hydrogen in the deposit from being freely dissipated during the "exposure" period.

In testimony whereof, I have signed my name to this specification this 7th day of August, 1919.

CHARLES P. MADSEN.