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METHOD OF FABRICATING METAL-COATED ARTICLES

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My present invention relates to methods of fabricating metal articles provided with surfaces of a "nickel metal", by which I mean either nickel, or cobalt, or alloys containing either or both of these metals. My invention relates more particularly to the fabrication of ferrous metallic objects provided with a composite layer or a plurality of layers of a "nickel metal", particularly nickel, and aims to provide metals of the general character specified above which are simple and convenient to practice, which are economical and which yield superior ferrous or other metal objects provided with impervious and mechanically sound and adherent surfaces of a "nickel metal", particularly nickel, especially in the form of a composite layer or a plurality of layers of such a metal. My invention relates, also, to the resulting products which are of a superior quality as regards the mechanical perfection and the degree of adherence of the composite layers or coatings of "nickel metal", such as nickel, to each other and to the metal base.

In the accompanying specification I shall describe several illustrative embodiments of the methods of the present invention. In the accompanying specification I shall also describe several illustrative embodiments of the products of the present invention, particularly the products resulting from the practice of the aforesaid illustrative embodiments of the methods of the present invention. It is, however, to be clearly understood that my invention is not limited to the specific embodiments thereof herein described for purposes of illustration only.

Referring to the aforesaid illustrative embodiments of the methods of the present invention, I may take a metal body, preferably a ferrous metal body, such as a portion of a spring steel bar intended to be fabricated into a resilient article, such as an automobile bumper. I now treat such an object as an anode in a bath of strong sulphuric acid, preferably sulphuric acid of a strength of more than about 84.5 per cent. For this purpose, I may use direct current, preferably with an external resistance in series equal to about five or six times the resistance of the cell itself. For the cathode I may employ either a sheet of lead or a sheet of iron or steel coated with lead, or, and preferably, a sheet of iron or steel itself. The acid should preferably be heated to a temperature of about 100° F. While an initial flow of current amounting to twenty (20) amperes, or more, per square foot of anode surface being treated may be used with considerable success, I may also employ current densities less than these, as down to ten (10), or even as low as five (5) amperes, or still lower, these initial current densities being calculated in amperes per square foot of anode surface being treated. With the lower current densities, however, a longer time of treatment is necessary than with the higher current densities.

Where the object being treated is a hollow article, such as a tank, vat, container, tube or the like, the acid is admitted to the interior of the container and the cathode inserted into the acid within the container. In such a case, also, if not enough acid is employed to entirely cover the interior surfaces desired to be treated, the hollow article containing the acid and the anode may be rotated in such a manner as to bring the acid into contact with all portions of the interior surfaces desired to be treated, in a manner which will be readily apparent to those skilled in the art to which the present invention relates.

The anodic treatment just described is continued until the flow of current drops to a fraction, as to one-fifth, or even less, of its initial value, at which point, which I characterize as the point of "passivation", it becomes substantially constant. This point, I have discovered, corresponds to the substantial removal of the surface carbon and occluded hydrogen from the metal object being treated. The object thus treated may now be rinsed in hot or cold wash water to remove the surplus acid.

I now provide the spring steel or other metal object so treated with a coating of nickel, preferably a coating of soft, mechanically perfect, ductile and malleable new nickel, such as is described and claimed in a co-pending application of Charles P. Madsen, Serial

No. 489,582, filed August 4, 1921, for "Means for electrodepositing metals". According to this process, while various types and compositions of baths may be used in the practice of the present invention, I prefer to use a bath of approximately the following composition:

Nickel sulphate	300 g.
Nickel chloride	25 g.
Boric acid	40 g.
Water	1 liter.

Having discovered that the presence of certain organic materials, such as dust, spores, bacteria, etc., has an undesirable effect on the deposit, I give the bath a preliminary treatment with an oxidizing and sterilizing substance, preferably in gaseous form, such as chlorine. Enough clorine is bubbled through the bath to oxidize the organic substances present therein and to convert any copper salts present in the bath as impurities to the insoluble cuprous chloride or oxychloride, but not enough to convert such cuprous chloride to the cupric chloride. Since, in making up the bath originally, an amount of alkali, such as caustic soda, but preferably nickel hydrate, has preferably been used in excess of what was necessary to neutralize the mineral acid present in the bath, thus precipitating ferrous hydrate from any iron salts present in the bath as impurities, the treatment with chlorine or its equivalent oxidizes this ferrous hydrate to the insoluble ferric hydrate, which may be readily filtered out of the solution. The bath is now filtered to remove the precipitates, principally ferric hydrate and cuprous chloride, and is now ready to receive the addition agent.

I have discovered that the presence of certain oxidizing agents, particularly hydrogen peroxide, in the bath during electrodeposition minimizes the formation of pores, pits and other mechanical imperfections in the deposited metal, an action due probably to the oxidation to water of any cathodic hydrogen and the conversion of the iron salts derived from the anodes to and their maintenance in the soluble ferric condition. For this purpose, I may add, for example, about 4 cc. of a 3% solution of hydrogen peroxide per liter of bath for each 24 hour run.

While a bath prepared and composed as above described will operate fairly well with the usual commercial types of anodes, I prefer to employ an anode of the following composition as being easy to fabricate and as being readily soluble, thus enabling the bath to be constantly maintained at its initial composition and rendering the process continuous and commercial. For this purpose I may pass air or other oxygen-containing gas through a molten mass of nickel in excess of the amount to which oxygen would be present in the usual commercial types of anode and up to a point where the black oxide of nickel (Ni_2O_3) appears on the surface of the molten mass, which latter is preferably free from such undesirable impurities as chromium, silicon and the like. Or I may add enough of a higher oxide of nickel, such as the peroxide (NiO_2), to accomplish the same result. The molten oxidized mass is now cast in chill molds into anodes of the desired shape, which anodes will be found to be highly soluble and remarkably suitable, mechanically, chemically and otherwise, for the intended purpose.

With the foregoing bath and anode, I now conduct the electrodeposition in any desired manner. Preferably, the bath is heated to a temperature of about 55° C. and a current density of about 5 amperes per square decimeter is used. With the means and under the conditions described above, deposits of any desired thickness, mechanically sound and perfect, may readily be obtained. The deposit, where pure nickel is deposited, as in the example given above, will be found to be free from pores, pits and other mechanical imperfections, and also to be substantially free from any occluded or combined hydrogen, so that the pure nickel deposit is remarkably malleable and ductile, and is also annealable. That is, the metal, whether or not it has previously been mechanically worked, may be heated to a red heat and annealed either slowly or quickly without embrittlement. Moreover, if the metal is annealed after it has been cold worked it will be softer than before.

To illustrate the ductility of this new metal, a strip one-sixteenth of an inch square which has been sawed off from a deposited sheet cathode may be cold drawn to a wire .002 of an inch in diameter without annealing, during which operation the strip is elongated from a length of about eight inches to a length of about 830 ft. The metal also has the unusual property of retaining, after cold working, considerable elongation power while acquiring a high degree of hardness. The Brinell factor of hardness will vary from about 63 to about 80, while the elongation factor is approximately 32% for the unworked deposit. Upon cold working the deposit whose hardness and elongation factors have just been given, as in the example of wire drawing given above, the Brinell factor of hardness increases to about 183, the tensile strength of the metal rises from 72,000 to 250,000 pounds per square inch, while the worked metal still retains an elongation factor of about 10%.

The nickel coating thus obtained will not only be remarkably workable and free from mechanical defects and imperfections, such as pores, pits and the like, but will also be found to adhere with remarkable tenacity to the spring steel or other ferrous metal base where the same has first been given the anode

treatment described above. I now subject the nickel-coated spring steel bar or other metal object to a mechanical working operation, which may include one or more successive annealing and tempering operations. It may here be stated that the processes of the present invention may begin at this point with the utilization of a spring steel or other ferrous metal object already provided with an adherent and mechanically sound and perfect coating of a readily workable "nickel metal", such as nickel. Where the coating is prepared and has the characteristics above described, its adherence and remarkable degree of workability readily lend themselves to the mechanical working and heat treating operations described above. It may here be stated that in another of its forms the process may commence at this stage, that is, where the nickel-coated spring steel or other ferrous metal object has already been mechanically worked to a certain shape, with or without heat treatments.

In this condition the object, as a result of the mechanical working and heat treating operations, may, in certain instances, be found to have developed certain mechanical imperfections. This may be due not so much to any defects of the "nicked metal", such as nickel coating, but may be due rather to the defects in the spring steel or other stock on which the coating was made or to imperfect mechanical working and heat treating operations. In any event, these imperfections, however they may be made, are obliterated and a perfect article obtained by subjecting the mechanically worked nickel-coated spring steel bar or other article to the following steps: I may subject the mechanically worked nickel-coated metal article, preferably after the same has been cleaned free from any grease or oxide, as by scrubbing the same with silicia sand by means of a brush and clean water, to the anode treatment described in detail above for the uncoated spring steel or other ferrous metal stock. The anodic treatment in this case should, however, be continued only for a comparatively short while, that is, until the "nickel metal", such as nickel, surface has been "finished" or rendered capable of receiving subsequent adherent coatings of "nickel metal", such as nickel. The time of this step of the treating operation should be carefully noted, which time may be readily determined by simple trial and experiment, to avoid any excessive dissolving action of the original "nickel metal", such as nickel, coating, which takes place under the action of the anodic treatment referred to above. This treatment seems to remove from the surface of the original "nickel metal", such as nickel, deposit the film of what is probably an oxide of nickel which ordinarily would prevent a subsequent deposit of "nickel metal", such as nickel, from being adherent to the original deposit. In any event, and since I do not wish to be limited to any particular theory or explanation of what appears to happen, I merely wish to state the result, which is that the subsequent "nickel metal", such as nickel, coating adheres with remarkable tenacity to the original coating.

In most instances since the second coating is placed on the nickel-coated or like article after the same has gone through the necessary mechanical forming and heat treating operations, the second coating need not be workable. In fact, I prefer that it shall consist of the hard variety of nickel described and claimed in the copending application of Charles P. Madsen, Serial No. 647,912, filed June 26, 1923, for "Method and means for electrodepositing nickel metals and the resulting products". While various types and compositions of baths may be used in the practice of the present invention, I prefer to use a "nickel metal" bath containing a fluorine compound, preferably a compound of nickel and fluorine, such as acid nickel fluoride, or nickel fluoborate. I find that this fluoride bath, especially when combined with the other features of the present invention, gives a superior result in operation and a better product.

For practical purposes it is not desirable to operate a bath containing either of these salts or compounds alone. Instead of this, the metal content of the bath is preferably principally supplied by a solution of nickel sulphate, in the proportion, preferably, of 300 grammes, per liter, to which about 10%, by weight, of either of the fluorine compounds designated above is added, calculated on the basis of the weight of the nickel sulphate used in the bath and containing the usual water of crystallization ($NiSO_4$, $7H_2O$).

I have discovered that a "nickel metal" electro-deposition bath, in order to yield mechanically perfect electrodeposited "nickel metal", such as pure nickel, or nickel alloys containing iron or hydrogen ~~or both~~ of these elements, as in the specific example of the product subsequently described in greater detail herein, and in order, also to avoid the formation of pits and similar mechanical imperfections in the resulting electrodeposited metal, should be substantially free from ferric compounds, particularly such compounds in solution in the bath. The bath should also preferably be free from ferric compounds in suspension, since these have a tendency to cause the resulting electrodeposited metal to be rough.

For this purpose I prefer to add to the "nickel metal" bath a reducing agent, preferably an organic reducing agent, such as oxalic acid, pyrogallic acid or hydroquinone, particularly the latter. The desired action of the reducing agent seems to result from its

maintaining the iron salts initially present in the bath or introduced therein by solution from the "nickel metal", such as the nickel, anode, which usually contains iron, in the ferrous rather than in the ferric condition, iron in the latter condition being apparently the principal cause of pits and similar imperfections in the deposited metal. The reducing agent, which may be used in a small amount, as will be readily indicated by trial and experiment, acts moreover, by maintaining the iron salts in the ferrous and therefore in the soluble condition, to deposit in perfect condition iron-nickel alloys, comprising the above-mentioned "hard" varieties of nickel containing iron in variable amounts, dependent upon the composition of the bath and the anode and their iron content.

While various anodes may be used for this purpose, I prefer to use a highly soluble anode, preferably a carbon-containing anode which may be made up as follows: To a molten mass of the "nickel metal", such as nickel, preferably free from silicon and chromium, I add an excess of carbon. Preferably the addition of carbon is effected to the molten mass in an electric or other furnace in a reducing atmosphere, the carbon used being preferably amorphous carbon low in ash content, such as a high grade gas coke. The carbon-containing metal is heated to a suitable temperature, as 1500° C., at which it will absorb the desired amount of carbon, being maintained at this temperature and frequently stirred for about half an hour. The metal is then carefully cooled to a point only a few degrees above its solidifying point and is then cast very quickly in iron or other chill molds. The result is a highly soluble and mechanically strong anode, remarkably well suited for the intended purpose.

With a bath and anode such as described above, deposits of "nickel metals", such as the hard varieties of "nickel metals" comprising the aforesaid iron-nickel alloys, may be made continuously and in perfect mechanical condition, being free from pits, pores and other mechanical imperfections. The deposits may contain anywhere from one-half to ten per cent of iron, more or less, dependent upon the conditions of electrodeposition and the composition desired for the product. The deposits will also ordinarily be found to contain traces of hydrogen.

Such deposits, as, for example, where they contain about one-half of one per cent of iron, are not only mechanically perfect, but, while being quite hard, as by having a Brinell factor of hardness of from about 182 to about 236, are quite ductile and may be readily worked without heat treatment and without embrittlement, being about as workable in the "cold" as ordinary Bessemer steel or brass. Such deposits are also remarkably strong, having a tensile strength substantially in excess of 72,000 pounds per square inch, the average tensile strength of the "soft" variety of pure electrodeposited nickel made in accordance with the invention described and claimed in another application of mine filed of even date herewith. In fact, deposits made in accordance with this invention often possess a tensile strength as high as 125,000, or even 136,000, pounds, or even more, per square inch, dependent upon their exact composition and the conditions surrounding their electrodeposition. By controlling the percentage of iron present in the bath and in the anode, and thus in the deposits, the strength and other properties of the deposits may in this way be varied within very wide limits for particular purposes.

This second coating will be found not only to be remarkably adherent to the original coating, but will also be found to yield a very high polish during any polishing or other finishing operation to which the second coating may be subjected. The two coatings, or where more coatings are employed, the plurality of coatings thus obtained will form a composite layer or coating, the several layers of which adhere to each other so as to form virtually a unitary layer of varying composition and mechanical properties from one elementary layer to the next. Of course, if desired, the second coating and also the other subsequent coatings, if such coatings are used, may, like the first coating, be of the soft variety of nickel and readily workable, but in such a case the final coating will not yield as high a polish, and where the subsequent coatings need not be mechanically worked the necessity for a workable coating vanishes and the hard coating, which yields a high polish, may be used instead.

The invention described above possesses many advantages for the intended purpose. The process is very simple to practice, quite economical, and results in a superior product for the intended purpose. By means of the second protective or finishing coating, especially in view of its adherence to the original coating, imperfections in the mechanically worked nickel-coated stock may be covered up and a perfect finished article obtained without consigning the original imperfectly finished article to the junk heap. The invention possesses other advantages in operation and in the properties of the resulting product which will readily occur to those skilled in the art to which the same relates.

What I claim as my invention is:

1. The method which comprises mechanically working a nickel-surfaced object, then treating the same as an anode in a bath of sulphuric acid and thereafter electrodepositing a fresh coating of nickel on the nickel surface so treated.

2. The method which comprises mechanically working a nickel-surfaced object, then

treating the same as an anode in a bath of sulphuric acid of a concentration of more than about eighty-five per cent. and thereafter electrodepositing a fresh coating of nickel on the nickel surface so treated.

3. The method which comprises mechanically working a nickel-surfaced metal object, then treating the same as an anode in a bath of sulphuric acid, and thereafter depositing on the object thus obtained a fresh surface of a "nickel metal".

4. The method which comprises mechanically working a nickel-surfaced metal object, then treating the same as an anode in a bath of sulphuric acid of a strength of more than about eighty-five per cent., and thereafter electrodepositing on the object thus obtained a fresh surface of a "nickel metal".

In testimony, whereof, I have signed my name to this specification this 20th day of December, 1924.

FRANK V. KNAUSS.