Patented Nov. 24, 1925. 1,562,711

UNITED STATES PATENT OFFICE.

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COATED METALLIC ARTICLE AND METHOD OF MAKING THE SAME.

No Drawing. Application filed July 27, 1920, Serial No. 399,387. Renewed February 10, 1925.

To all whom it may concern:

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

My invention relates to the production of coated metallic articles of manufacture, and particularly to the production of coated sheets or other forms which are afterwards shaped, although also applicable to shaped articles. My invention relates also to methods of producing articles of the classes above specified. While my new articles of manufacture may consist of any metallic base or body, particularly valuable results are obtained with my present invention when the base or body receiving the coating consists of steel or iron.

Moreover, while the coating may be of various metals or metallic alloys, such as nickel, tin, or lead, applied by any suitable means, as by melting, spraying or by electrodeposition, particularly valuable results may be obtained with the use of my present invention in connection with coating materials consisting of one of the "nickel metals", particularly where such metals are applied by electrodeposition. It may here be stated that by "nickel metals" I mean to designate either nickel or cobalt, or alloys containing substantial amounts of either or both of these metals.

By way of example, I shall in the accompanying specification describe illustrative embodiments of my present invention, it being understood, however, that my present invention is not limited to the illustrative embodiments which are herein set forth for the purposes of illustration only.

Before describing in detail the illustrative embodiments of my invention referred to above, it may be useful to briefly outline the prior state of the art to which the present invention belongs, and to briefly indicate the probable theory of the action of the process of the present invention, although it is clearly to be understood that I do not wish in any way to limit myself to any particular explanation of the theory of the action of the present invention.

There is considerable difference of opinion as to the degree of adherence of coatings of various metals as applied by the ordinary methods to iron or steel which has been treated by the customary or usual cleaning processes. But it is generally admitted that no close adherence, amounting to an alloy union, is obtained between the steel base and the coating metal, except possibly in the case of tin, applied hot. This difference of opinion probably arises from the fact that the previous investigators have not taken into account the effect of the thickness of the coating upon its degree of adherence. I have discovered, among other things, in connection with the development of the present invention, and taking the case of nickel applied by electrodeposition, for example, that coatings less than a certain critical thickness, which is between about two ten-thousandths and about three ten-thousandths of an inch, when applied to steel or iron treated by the ordinary cleaning methods, adhere much more closely than coatings which are greater in thickness than the critical thickness specified, although such coatings do not constitute true alloy unions.

It is, however, clearly understood that electrodeposits of a metal of a thickness below about two ten-thousandths to about three ten-thousandths of an inch are all porous, a coating of these thicknesses being the ones which I have discovered possess a slight degree of adherence already referred to. That is, taking the case of electrodeposited coatings, for example, such coatings on steel, treated by the ordinary cleaning methods, are porous up to the critical thickness of about three ten-thousandths of an inch. But when applied in a sufficient thickness to make the coating relatively impervious, I find that such coatings lose the slight adherence which coatings, of less

thickness than the critical thickness referred to, possess. The thicker coatings, as coatings from about five to about ten ten-thousandths of an inch, or greater, in thickness, while less pervious, or even entirely impervious, have little or no adherence to the steel or other bases to which they may be applied, and are readily separable from such bases. In the case of coatings of the "nickel metals", such coatings, as obtained by the ordinary methods of electrodeposition, are furthermore brittle and unworkable, and so expensive as to render the same commercially valueless.

No satisfactory explanations of these various phenomena have hitherto been offered, and while I do not wish to be limited to any particular theory of the cause of these phenomena, it is my present opinion that coatings below the critical thickness for any particular metal, as between about two ten-thousandths and about three ten-thousandths of an inch, in the case of nickel applied by electrodeposition, follow the surface crystal structure of the steel or other base to which they are applied, and thus tend to adhere to the separate crystals of the surface of the base, with a consequent tendency to leave spaces or rifts at the boundaries of the crystals on the surface of the base. But when the thickness of the coating is increased, as to about five ten-thousandths to about ten ten-thousandths of an inch, or more, as in the case of nickel applied by electrodeposition, for example, the coating, the exact character of which otherwise depends on the factors of deposition, tends to assume its own physical form, independently of the form or character of the surface to which its is applied, and builds up its own crystal structure independently of the crystal structure of the surface of the base, with a consequent tendency in the coating to become unitary and homogeneous, and at the same time to draw away from, or separate from, the base.

I have discovered that by treating the surface of the iron, steel or equivalent object to be coated by the method set forth in my co-pending application, Serial Number 399,386, filed July 27, 1920, the surface of the iron, steel or equivalent base is so modified that the deposit applied thereto, as in the case of a "nickel metal" applied by electrodeposition, does not tend, even in thicknesses less than the critical thickness referred to above, to follow the surface crystal structure of the base, but tends rather, from the very start, to assume an independent, homogeneous and impervious structure, and to render the coating applied to a base treated by the method referred to not only impervious down to the very smallest thicknesses, but also remarkably adherent, even in thicknesses greatly exceeding the critical thickness referred to above. So strong is this adherence that it has led me to believe that the junction between the base and the coating is probably an alloy union. I have further discovered that by combining the method for treating the iron, steel or equivalent base referred to above, with the method for depositing "nickel metals" described and claimed in my co-pending applications, Serial No. 254,793, filed September 19, 1918, Serial No. 292,793, filed April 26, 1919, and Serial No. 292,794, filed April 26, 1919, I may obtain a "nickel metal" coating which is not only impervious for thicknesses far less than the critical thickness referred to above, and adherent for all thicknesses, even for thicknesses far greater than the critical thickness referred to above, but which is also malleable and workable to a remarkable degree, so that unshaped or partially shaped articles, coated with a "nickel metal" in accordance with the present invention, may readily be shaped and worked without danger of the coating separating from its base, or breaking during the working or shaping operation.

Referring to the illustrative embodiments mentioned above, I may use for the object to be coated a sheet of iron or steel, preferably the latter. Before the coating metal is applied, I treat the surface of the sheet of steel, for example, to adapt the same to receive a closely adherent, impervious coating of metal, particularly of a "nickel metal", as nickel, of the character above set forth, in accordance with the treating process set forth in my copending application, Ser. No. 399,386, filed July 27, 1920, referred to above, and entitled "Method of treating metals, and resulting products".

This method, briefly, comprises using the sheet steel, or other metal object which is to receive the coating of metal, as an anode in a bath of strong sulphuric acid, this bath preferably being heated to a temperature above normal, as between about 100° F. and 130° F., preferably about 130° F. For the cathode I may use either another sheet of steel or, and preferably, a sheet of lead. It is desirable that the sulphuric acid bath should be of a strength of more than about 86%. In particular, I find that sulphuric acid of about 92% strength, or even anhydrous, or substantially anhydrous, as 96%, sulphuric acid, is very desirable for the treatment of the surface of a steel sheet or equivalent object preparatory to receiving the coating of metal.

The polarization balance voltage of such a cell, operating at a temperature of about 130° F., which voltage is equal to the back voltage, or counter-electromotive force generated by the cell when it reaches a condition of equilibrium, which will be in about 15 seconds after it has been put into opera-

tion, is about 24 volts. I prefer to use an overvoltage in excess of the polarization balance voltage referred to, and amounting to a line voltage of about 42 volts. This results in an initial current density of about 100 amperes per square foot where a temperature of about 130° F., for example, has been employed. In about 15 seconds the cell, after a brief and initially slight increase in current density, will be found to have reached a state of equilibrium with a diminution in the flow of current from the initial flow of about 100 amperes per square foot to a flow amounting to about one-sixth of this value, or about 17 amperes per square foot. After this condition of equilibrium has been attained, the treatment is continued for a length of time dependent upon the concentration of the acid in the bath, and amounting to an additional period of treatment equal to about 180 seconds where an acid of 86% strength has been employed, or to about 60 seconds where an acid of about 92% strength has been employed, and to about 15 seconds where an acid of about 96% strength has been employed, making a total period of treatment of 195, 75 and 30 seconds, respectively.

The surface thus treated will be found to be free from grease, vegetable, animal and mineral oils, and to be adapted to render the subsequent coating remarkably sound, and adherent. Part of this desirable condition of the surface of the metal is, however, comparatively temporary, especially in so far as the desirable property of adherence is concerned, although substantially permanent in so far as the desirable property of the imperviousness of the resulting coating is concerned. Although I do not wish to be limited to any particular theory of the explanation of this phenamena, it is my present belief that the disappearance of the desirable property of adherence by exposure of the treated surface to the air, is due to the probable fact that the adherence is a function of the oxidation characteristics of the surface to be coated, my treatment probably causing a reduction of the oxides on the surface of the metal to be coated, and thus permitting close adherence amounting even to an alloy union between the base and the coating, so long as the surface of the base is in its original reduced condition. The impervious character of the coating is, on the other hand, probably the result of the changed character of the crystal surface of the iron or steel base, which surface is probably, by my treatment, deprived of part or all of its original surface carbon content, and appears to be partially or wholly converted into ferrite. It is therefore preferred that the metal should be at once coated by being placed in the deposition bath, preferably within about a minute after it has been treated, as above set forth, and its surface rinsed in water. The above-described characteristics of the surface of the object to be coated may, however, be partially preserved by keeping the metal under distilled water, or in a 10% solution of sodium cyanide.

Where the metal base, as sheet steel, has a large amount of oxide on it, it may be given a preliminary pickling treatment to remove the oxide. For example, I may use a pickling bath consisting of a 20% solution of sulphuric acid containing about 5 grams of wheat flour per liter, and maintained at a temperature of about 180° F. The metal is kept in the pickling bath for about two minutes, after which it is subjected to the cleaning treatment described above.

I have discovered that my cleaning treatment successfully counteracts and overcomes the usual undesirable consequence of the ordinary pickling step, the ordinary pickling operation rendering the object subjected to the pickling step brittle and the subsequent coatings even more porous than coatings of the same thickness on unpickled stock. My process, on the other hand, restores the object which has been subjected to the pickling process to its initial workable, unbrittle condition, and renders the subsequent coatings impervious and adherent, notwithstanding the preliminary pickling treatment.

I now provide the steel or equivalent object, treated as above set forth, with a dense, reguline, workable coating of a "nickel metal", preferably by the method disclosed in my co-pending application, Serial Number 292794, filed April 26 1919. By way of example, I shall briefly describe the process of the application last cited as applied more particularly to nickel in the provision of a nickel-coated sheet of steel, the coating of which is dense and impervious, being free from pores and pits, and workable to a remarkable degree. This coating is also so strongly adherent to the steel base to which it is applied, especially where the steel base has been subjected to the cleaning treatment described above, that it cannot be separated from its base nor can the base be separated from the coating short of the breaking strength of the coating and coated metals, respectively.

The process of electrodepositing the nickel is briefly as follows: For my anode I prefer to employ a nickel anode which is substantially free from occluded or combined gases, such as oxygen, and is also substantially free from chromium, copper and silicon, and also from "passive" or insoluble portions. Such an anode, which is substantially completely soluble, contains amphorous carbon and may be prepared by melting nickel "shot," or other variety of nickel, in a reducing atmosphere, such as in an atmosphere of carbon

monoxide, together with from about .5 to about 2 per cent of amphorous carbon. The mixture should be stirred occasionally while in a molten condition and kept molten from about one-half to about one hour, care being taken that the temperature is not raised to such a point as to graphitize the amphorous carbon. In casting such anodes, care should also be taken not to let the cast cool too rapidly, since it is desirable to prevent the formation of comparatively large crystals, the anode being better in operation where it is of a fine crystalline structure, with the average longest dimension of the crystals approximately between one-sixty-fourth and one-sixteenth of an inch.

While various electrodeposition baths may be used in connection with the present invention, I prefer to use a bath made up of nickel chloride ($NiCl_2$), nickel sulphate ($NiSO_4$), boric acid and a slight amount of sodium sulphate. This bath is preferably maintained at a temperature of about 130° F. Such a bath, in order to deposit perfect metal, should also contain a comparatively large amount of non-nickel-solvent hydrogen (H)-ion or acid concentration, provided by means of the boric acid, already referred to, together with a substantial amount of finely divided, suspended, as collodial, "nickel metal" hydrate, as nickel, preferably nickelous, hydrate, which hydrate is apparently, at the temperatures ordinarily employed, not attacked by the boric acid present in the bath and is, under proper deposition factors more fully set forth hereinafter, slowly and continuously generated during the operation of the bath. The hydrate in the bath is also not attacked, at the temperatures ordinarily employed, by the low solvent-acid concentration of the bath which I have discovered should be maintained in the bath in order to deposit perfect metal. This solvent-acid H-ion concentration, ordinarily provided by the presence of very small quantities of either free sulphuric or free hydrochloric acid in the bath, is so minute, however, that no ordinary acid indicator, such as the usual dye indicators, will detect its presence. The exact amount of free acid which should be present for effecting a particular result may, in any case, be readily determined by trial and experiment.

In order to maintain the bath in continuous operation, there should, I have discovered, be a predetermined ratio between the area of the anode and the area of the cathode, particularly in the case of the anodes described above, whereby it is possible to maintain the initial free solvent-acid concentration of the bath substantially constant during continuous operation. It may here be stated that in calculating the "anode-cathode ratio," the ratio taken is that between the area of the surface of the cathode and the total area of the surface or surfaces of the anode or anodes facing the cathode, plus the area of the edges of such anode or anodes. On this basis and with a ratio of anode to cathode of 1 to 1, I have maintained the bath at its initial solvent-acid concentration for several weeks of continuous operation. If the "anode-cathode ratio" is too large, as 2 to 1, or greater, the bath has an acid-tending characteristic and the deposit will absorb free hydrogen or acid and tend to become hard, and even brittle. If the "anode-cathode ratio" is too small, as ½ to 1, or less, the bath will have an alkaline-tending characteristic with a consequent generation of an excess of free hydrate which will tend to be absorbed by the deposit and to also render the same hard, and even brittle.

While the "still bath process" of deposition described above is suitable in some cases, in other cases and especially where a coating of great thickness is desired, and also in those cases where it is desired particularly to minimize all danger of pores or pits, or of other imperfections in the deposited coating, I prefer to combine the "still bath method" described above with the mechanical or equivalent manipulation of the cathode with respect to the bath as set forth in my co-pending applications Serial Number 254,793, filed September 19, 1918, and Serial Number 292,793, filed April 26, 1919. This mechanical manipulation may comprise exposing the deposited metal on the cathode intermittently to a gaseous, preferably an oxidizing, medium, such as air, for a period of time less than a certain "maximum" period, beyond which the deposit which would form during the next period of deposition would tend to be separable, but greater than a certain "minimum" period, under which the hydrogen liberated at the cathode during any one period of deposition would not have sufficient time to escape before the cathode is returned to the bath for the next period of deposition. In the case of nickel, and working with a current density of about 50 amperes per square foot, in a very nearly neutral bath, at a temperature of about 130° F., the period of exposure may be varied between about 2 and about 15 seconds, with a deposition period varying between about 30 seconds and about 10 minutes.

While deposits of varying thickness may be made in practising the method described above, I have found that where the steel or equivalent object is cleaned and thereafter coated in accordance with the procedure described above, I may obtain impervious coatings of perfect metal which are as thin as one-half of a ten-thousandth of an inch, or even less, as proven by the standard "ferroxal" test. I have even made coatings as thin as one one-hundred-thousandth of an inch

in thickness which are useful and more nearly impervious than coatings of three ten-thousandths of an inch in thickness made by the old method. Such coatings, which may be made by a 15 second deposit where a current density about 100 amperes per square foot is employed, will also be found to be dense and reguline, and remarkably malleable and ductile. The workability of the coated sheet steel or other object may readily be demonstrated by bending, punching, and seaming the coated sheet. I have also found that coated sheets made in accordance with the method described above, may readily and successfully be spot welded and soldered by means of the usual solders without the use of a flux. The coating metal being of nickel, the coated object does not tarnish, and maintains a bright, clean, metallic surface which is strongly resistant to the corrosive action of most chemicals and of the usual weathering agents.

The adherence of the coating to the steel or other base to which the coating is applied is remarkable. For example I have applied to a sheet steel base having a thickness of about one-fortieth of an inch a nickel coating of equal thickness, by the method set forth above. I have found that in such a case the coating metal could be separated from the coated metal only by chiseling the same apart, or by a similarly severe operation. Thereafter I found that I could not effect a further separation of the coating from the base, as the pull necessary to effect a further separation exceeded the strength of the steel base.

Two of the phenomena which show that my new cleaning treatment produces a change in the surface condition of the steel, and which are more noticeable in the case of steel which has been pickled, are: First, that the surface of the steel has an entirely different appearance to the eye from any other steel, treated or untreated, and especially from the same steel after pickling, being much whiter and more pearly; and second, that in electrodepositing upon such treated steel, a condition which is particularly noticeable in the case of a thin deposition, the deposited coatings of a clear, metallic-like lustre are formed upon the steel almost instantly, often within one or two seconds, whereas in the case of steel, not so treated, and particularly the case of pickled steel, the initial deposit is black, later becoming dark grey and then light grey, attaining a uniform, metallic appearance only after one or two minutes under the usual conditions.

It is of course to be understood that my invention is not limited to the particular embodiments thereof herein set forth, for purposes of illustration only.

What I claim is:

1. As an article of manufacture, a flexible metal base provided with an adherent, workable electrodeposit of a "nickel metal."

2. As an article of manufacture, a steel base provided with an adherent, workable electrodeposit of a "nickel metal."

3. As an article of manufacture, a sheet steel base provided with an adherent, ductile and impervious electrodeposit of a "nickel metal."

4. As an article of manufacture, a metal object provided with a closely adherent, workable and impervious electrodeposit of nickel.

5. As an article of manufacture, a sheet of metal provided with a closely adherent, workable and impervious electrodeposit of nickel.

6. As an article of manufacture, a sheet metal base, provided with an impervious deposit of "nickel metal" of a thickness less than about three ten-thousandths of an inch.

7. As an article of manufacture, a flexible sheet metal base, provided with an impervious deposit of "nickel metal" of a thickness less than about three ten-thousandths of an inch.

8. As an article of manufacture, a sheet steel base provided with an impervious deposit of "nickel metal" of a thickness less than about three ten-thousandths of an inch.

9. As an article of manufacture, a flexible sheet steel base provided with an impervious deposit of "nickel metal" of a thickness less than about three ten-thousandths of an inch.

10. As an article of manufacture, a metal object provided with an impervious deposit of nickel of a thickness less than about three-ten-thousandths of an inch.

11. As an article of manufacture, a steel object provided with an impervious deposit of nickel of a thickness less than about three ten-thousandths of an inch.

12. As an article of manufacture, a sheet of metal provided with an impervious deposit of nickel of a thickness less than about three ten-thousandths of an inch.

13. As an article of manufacture, a sheet of steel provided with an impervious deposit of nickel of a thickness less than about three ten-thousandths of an inch.

14. As an article of manufacture, a metal base provided with a closely adherent deposit of "nickel metal" of a thickness greater than about three ten-thousandths of an inch.

15. The method of providing an iron, steel or equivalent base with an adherent, impervious, workable coating of "nickel metal," which comprises treating said base as an anode in a bath containing sulphuric acid of between about eighty-six per cent and about

ninety-six per cent strength, while maintaining the bath at a temperature of between about one hundred and about one hundred and thirty degrees Fahrenheit, impressing on the cell a line voltage of about forty-two volts for a period of time substantially in excess of the time required for the cell to reach a condition of equilibrium, and thereafter electrodepositing on the base so treated an impervious, adherent, workable layer of "nickel metal" by electrodeposition.

In testimony whereof, I have signed my name to this specification this 23rd day of July, 1920.

CHARLES P. MADSEN.