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METHOD OF TREATING METALLIC OBJECTS AND RESULTING PRODUCTS.

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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 Methods of Treating Metallic Objects and Resulting Products, of which the following is a specification.

My invention relates to methods of treating metallic objects to enable the same to receive closely adherent and impervious coatings of various metals in various thicknesses, by means of various coating processes, and to the products resulting from the application of such methods. My invention finds particularly successful application in the treatment of metallic sheets, usually of iron or steel, preferably of steel, to enable the same to afterwards receive adhesive and impervious metallic coatings of such character as to enable the coated sheets to be afterwards shaped, although my invention is also applicable to shaped or partially shaped articles.

For purposes of illustration I shall describe, in the accompanying specification, one form of my invention as more particularly applied to the treatment of iron or steel objects, preferably objects of steel, and more particularly in the form of steel sheets, in order to enable such steel sheets to receive adherent, impervious coatings of metal. While various means of applying the metallic coating may be employed, such as melting, spraying, or electrodeposition, I shall, in connection with the illustrative embodiment of my invention herein set forth, describe the same as applied in connection with the coating of metals by electrodeposition. Moreover, while coating metals of varying composition may be employed, such as nickel, tin, lead or zinc, I shall in the accompanying specification, by way of example, describe the use of zinc as the coating metal, it being understood, however, that my invention is not limited to the illustrative embodiments thereof which are herein set forth for purposes of illustration only.

Before describing in detail the illustrative embodiments of my invention referred to above, I shall briefly outline the prior state of the art to which the present invention belongs and shall briefly indicate the probable theory of the action of the process of the present invention, it, however, being clearly understood that I do not wish in any way to limit myself to any particular theory which I may now hold as to the action involved in, and the principles underlying, the process 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 usual cleaning processes, as by the usual chemical or electrochemical pickles. It is generally admitted, however, that no close adherence amounting to an alloy union is obtained between the steel or equivalent base and the coating metal, except possibly in the case of tin, applied hot. This difference of opinion probably arises from the fact that previous investigators have not taken into sufficient account the effect of the thickness of the coating upon its degree of adherence. I have discovered, among other things, that coatings less than a certain critical thickness, which varies for the various metals, and which in the case of nickel, applied by electrodeposition, for example, is between about two ten-thousandths and 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 in the case of nickel, although such coatings do not constitute true alloy unions. By "critical thickness" I mean such thickness for the electrodeposited coating that if such thickness is exceeded, the coating is impervious but non-adherent, while if such thickness is equalled or if the thickness of the electrodeposited coating is less than such "critical thickness," the coating is adherent but is pervious.

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

a sufficient thickness to make the coatings relatively impervious, I find that such coatings lose the slight adherence which coatings of less thickness than the critical thickness referred to generally possess. The thicker coatings, as coatings from about five to about ten ten-thousandths of an inch or greater in thickness in the case of nickel, for example, 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.

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 involved in and the principles underlying these phenomena, it is my present opinion that coatings below the critical thickness for any metal, as between about two ten-thousandths and about three ten-thousandths of an inch in the case of nickel for example, applied by electrodeposition, to take a particular example of one of the numerous methods of coating one metal with another, follow the surface crystal structure of the steel or equivalent bases to which they are applied, and tend to adhere to the separate crystals of the surface of the bases, with a consequent tendency to leave spaces or rifts at the boundaries of the crystals on the surface of the bases. But where the thickness of the coating is increased, as to about five ten-thousandths to about ten ten-thousandths of an inch or more in thickness, as in the above example of nickel applied to the base by electrodeposition, 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 it 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 to which it is applied.

I have discovered that by treating the surface of the iron or steel or equivalent object to be coated in accordance with the method of the present invention, as more fully set forth hereinafter, the surface of the iron, steel or equivalent base is so modified that the deposit applied thereto, as in case of nickel or zinc applied by electrodeposition, does not tend, even in thicknesses less than the critical thickness defined 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 subsequently set forth not only impervious down to the very smallest thicknesses, but also remarkably adherent, even in thicknesses greatly exceeding the critical thickness as defined 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 one. I have further discovered that by combining the method for treating the iron, steel or equivalent base as more fully set forth hereinafter, with the method of coating with zinc, particularly by electrodeposition, more fully set forth hereinafter, I may obtain a zinc coating which is not only impervious for thicknesses down to one-half of one ten-thousandth of an inch, and adherent for all thicknesses, even for thicknesses much in excess of the critical thickness of zinc, which is from about two to about three ten-thousandths of an inch, but which is also malleable and workable to a very great degree, so that unshaped or partially shaped articles coated with zinc in accordance with the present invention may be readily 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 of my invention mentioned above, which are herein set forth for purposes of illustration only, I may use for the object to be coated a sheet of steel or iron, preferably the former. I now treat the iron or steel sheet according to the method of my present invention. 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 to 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, resistance balance voltage generated by the cell when it reaches a condition of equilibrium, which will be in about 15 seconds after it has been put into operation, 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 phenomena, 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 its original surface carbon content, and appears to be 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 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.

I have discovered that my cleaning treatment successfully counteracts and overcomes the usual undesirable consequences 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 thicknesses 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 zinc by any suitable method for electrodepositing zinc. Preferably I employ the following method of electrodepositing the zinc on the iron or steel object, since I have discovered that this method co-operates with remarkable efficiency with my above-described method of treating the iron or steel object in the production of a coating which is impervious down to the smallest thicknesses and remarkably adherent. For this purpose I may employ a zinc bath containing, for each liter of electrolyte, three normal equivalents or approximately 242 grams of zinc sulphate ($ZnSO_4$), calculated in the dry state, $\frac{1}{10}$ of a mol. or 6.2 grams of boric acid (H_3BO_3), and $\frac{2}{10}$ of a mol. or 36 grams of dextrose ($C_6H_{12}O_6$). The solution is preferably worked cold, that is, at normal temperatures, with a current density approximately equal to 14 amperes per square foot of cathode surface. Any suitable zinc anode may be used.

The thickness of the coating applied as above set forth of course depends on the ultimate use to which the coated object is intended to be applied. Where the iron, steel or equivalent base has been treated in accordance with the method of my present invention, as above set forth, I have found that coatings of zinc, applied as herein set forth, or by any equivalent method for electrodepositing zinc, or by otherwise applying the zinc to the base, in thicknesses down to one-half of one ten-thousandth of an inch, are impervious, while at the same time being very closely adherent. So close-

ly adherent are such coatings, in fact, that I am inclined to believe that the union between the zinc coating and the iron, steel or equivalent base practically amounts to an alloy union. I have further discovered that the coating may be made much thicker without in any way undesirably affecting its adherent qualities. For example, I have applied to a sheet steel base having a thickness of about 1/50 of an inch, a zinc coating of equal thickness, by the methods above set forth, and have found that in such a case the coating metal could be separated from the coated metal or base only by chiseling the same apart, or by some 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 coating metal, in this case zinc.

The imperviousness of the coated metal may be demonstrated by any of the standard tests for porosity, which tests, when properly applied, will indicate that the coating, when made in accordance with the method of my present invention, is impervious down to remarkably small thicknesses. The workability of the coated sheet steel or other object made in accordance with the present invention, may readily be demonstrated by bending, punching and seaming the coated sheet. I have also found that sheets coated with zinc, in accordance with the method described above, may readily and successfully be soldered by means of the usual solders without the use of a flux. The coating being, in the example here given, of zinc, and being impervious down to the very low limit of one ten-thousandth of an inch, not only gives an ornamental and highly attractive appearance to the metal base to which the same is applied, but also efficiently protects the same from rusting and from the action of the usual weathering agents. Furthermore, where the coating of zince is applied by electrode deposition in accordance with the method above set forth, the coating will be found to possess an exceedingly fine grain, resulting in a fine, smooth coating, having unusual lustre and being unusually attractive in appearance.

Two of the phenomena which further 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 electrode depositing 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 which are herein set forth for purposes of illustration only.

What I claim is:

1. The method of preparing iron, steel or equivalent surfaces to receive adherent and impervious metallic coatings, which comprises making the object to be coated the anode in a bath containing sulphuric acid of more than about eighty-six per cent strength while maintaining the bath at a temperature above normal.

2. The method of preparing iron, steel or equivalent surfaces to receive adherent and impervious metallic coatings, which comprises making the object to be coated the anode in a bath containing sulphuric acid of about ninety-two per cent strength while maintaining the bath at a temperature above normal.

3. The method of preparing iron, steel or equivalent surfaces to receive adherent and impervious metallic coatings, which comprises making the object to be coated the anode in a bath containing sulphuric acid of more than about eighty-six per cent strength while maintaining the bath at a temperature above about one hundred degrees Fahrenheit.

4. The method of preparing iron, steel or equivalent surfaces to receive adherent and impervious metallic coatings, which comprises making the object to be coated the anode in a bath containing sulphuric acid of more than about eighty-six per cent strength while maintaining the bath at a temperature of about one hundred and thirty degrees Fahrenheit.

5. The method of preparing iron, steel or equivalent surfaces to receive adherent and impervious metallic coatings, which comprises making the object to be coated the anode in a bath containing sulphuric acid of more than about eighty-six per cent strength, and impressing on the cell a line voltage substantially in excess of the polarization balance voltage of the cell.

6. The method of preparing iron, steel or equivalent surfaces to receive adherent and impervious metallic coatings, which comprises making the object to be coated the anode in a bath containing sulphuric acid of more than about eighty-six per cent strength, and impressing on the cell a line voltage sub-

stantially in excess of about twenty-four volts.

7. The method of preparing iron, steel or equivalent surfaces to receive adherent and impervious metallic coatings, which comprises making the object to be coated the anode in a bath containing sulphuric acid of more than about eighty-six per cent strength, and impressing on the cell a line voltage of about forty-two volts.

8. The method of preparing iron, steel or equivalent surfaces to receive adherent and impervious metallic coatings, which comprises making the object to be coated the anode in a bath containing sulphuric acid of more than about eighty-six per cent strength, impressing on the cell a line voltage substantially in excess of the polarization balance voltage of the cell, and maintaining said impressed voltage for a substantial time after the cell reaches a condition of equilibrium.

9. The method of preparing iron, steel or equivalent surfaces to receive adherent and impervious metallic coatings, which comprises making the object to be coated the anode in a bath containing sulphuric acid of more than about eighty-six per cent strength, impressing on the cell a line voltage substantially in excess of about twenty-four volts, and maintaining said impressed voltage for a substantial time after the cell reaches a condition of equilibrium.

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

CHARLES P. MADSEN.