

## UNITED STATES PATENT OFFICE

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## PROCESS OF COATING METALS

No Drawing.

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This invention relates to the coating or surface treating of metals, such as iron, which are susceptible to corrosion. The term "corrosion" as here used is to be understood as a general term including not only ordinary rusting of the metal at low temperatures but also oxidation at high temperatures.

One object of this invention is to produce a protective coating for a metal susceptible to corrosion which will effectively protect the metal surface and which will be resistant to and withstand the action of oxidizing media at high temperatures.

Another object of this invention is to produce such a coating at a lower temperature than has previously been done.

Still another object is to effect such a coating with chromium in the atmosphere of an ordinary electric furnace.

A chemical element may be caused to diffuse into a mass of metal to be coated at a temperature below the melting point of the metal and it has been found that when a metallic substance, such as chromium, is brought into surface contact with a foundation metal, such as iron, molybdenum, or tungsten, the metal forming the coating enters the surface of the foundation metal below the melting point of either metal and forms a layer of alloy. In such a process, however, the temperature employed must be very high (about 1200° C. to 1350° C.) and at such elevated temperatures a coating metal, such as chromium, becomes oxidized and can not readily diffuse into the metal to be coated. Non-oxidizing conditions must, therefore, exist so that this process must take place either in an atmosphere of a reducing gas, such as hydrogen, or in an atmosphere of an inert gas, such as nitrogen, or in a vacuum.

I have found, however, that if a metal, which has a relatively low melting point and which is lower than the melting point of the coating metal, and which has an affinity for the foundation metal, is used with the coating element, I can apply a protective coating at a comparatively low temperature. Such coating will besmooth and even and will withstand corrosion for a relatively long period. For example, I have found that zinc used with

chromium gives a fine homogeneous coating consisting mainly of chromium on iron at a temperature of 900° C. In carrying out this process chromium powder and granular zinc are used and heated in contact with the iron in a suitable electric resistor furnace. The proportions of zinc and chromium which may be used range from about 5 to 20% by weight of zinc, and from about 95% to 80% by weight of chromium. A mixture which I have found gives good results is about 10% zinc, by weight, and about 90% chromium, by weight. During this process it is found that zinc vapor is given off during heating, the rate reaching a maximum at about 890° C. This zinc vapor which is given off surrounds the metal to be coated and acts as an oxidation preventative medium. In its presence the chromium will not be oxidized.

I have found also that the addition of a metal, such as aluminum, to a mixture of chromium and zinc will aid in the process of coating. This process, as well as when zinc and chromium alone are used, may be carried out in the ordinary electric furnace atmosphere, thus dispensing with an inert or reducing atmosphere.

A mixture which I prefer to use, although the exact proportions are not to be understood in a limiting sense, for, as will be pointed out, the range may be varied, is about 10% by weight of zinc, about 5% by weight of aluminum and about 85% by weight of chromium. The percentage of zinc can be varied and any amount up to 20% by weight has been found to be satisfactory. The percentage of aluminum and chromium used may also be varied. The mixture containing about 10% of zinc by weight gives very good results. This mixture, when heated in contact with the metal to be coated, I have found gives a very uniform coating of chromium on cold rolled or black iron specimens. Microscopic cross sections of coated specimens showed a very good intermediate alloy of chromium and iron.

In coating chromium on iron I found that an iron content of about 1.5% in the chromium had a good effect. In one case the following proportions were found desirable and used,

about 10% by weight of zinc, about 5% by weight of aluminum, about 42.5% by weight of iron-free chromium and about 42.5% by weight of iron-bearing chromium having an iron content of about 3%. The proportions here used may also be varied as pointed out above. Pieces of cold rolled iron  $\frac{1}{8}$  inch in diameter and 3 inches long were used. The iron coated with this mixture was heated in a suitable electric resistor furnace. Volatilization of the zinc was plainly noticeable in the furnace air atmosphere and the temperature was allowed to reach 925° C. to thoroughly drive off the zinc.

This treatment increased the diameter of the iron by .048 inch and one sample was in good condition after heating for 100 hours at 1100° C. to 1150° C. Salt spray tests on  $\frac{1}{8}$  inch by  $\frac{3}{4}$  inch by 3 inches cold rolled specimens chromized similarly and ground smooth on a broad surface, showed better resistance to corrosion than chromium electroplated directly on iron.

The results of my demonstrations show that heavier, homogeneous, and more resistant chromium coatings may be applied with the aid of zinc and aluminum, that a much lower temperature to obtain the coating may be used than has heretofore been the case and that the coating may be applied in the ordinary furnace air atmosphere without any danger of oxidation. I have also chromized other metals besides iron in a similar way and as examples of such metals I mention tungsten and molybdenum.

While I have up to this point described my invention as applied to chromium it is by no means limited to the use of this metal alone. As an example of the broad application of this process I mention the coating of iron with aluminum. One method I prefer to use is as follows:

A strip of black iron about .060 inch thick is placed in an iron tube with one end closed and surrounded with a mixture consisting of about 30% aluminum by weight, about 5% zinc oxide by weight, and about 65% aluminum oxide ( $Al_2O_3$ ) by weight. The proportions just indicated are merely by way of example. The proportions of aluminum, zinc and alumina may be varied within the following limits when a stationary retort is used: 20 to 40% aluminum by weight, 3 to 10% zinc oxide by weight, 77 to 50% alumina by weight; for a revolving retort 15 to 20% aluminum by weight, 1 to 5% zinc by weight, 84 to 75% alumina by weight. In a revolving retort zinc is used instead of zinc oxide so that zinc vapor may be obtained since the zinc oxide would have no effect until it was reduced by reaction with the aluminum. The tube containing the iron specimens, after being plugged at the open end with asbestos paper, is fired for about three hours at about 1000° C., or slightly below this temperature,

in a suitable electric resistor furnace with a hydrogen atmosphere. A sample .060 inch thick so treated measured .066 inch after being coated. For an accelerated oxidation test it was heated in air at 1100° C. for 24 hours together with a sample of iron coated by a method heretofore employed, which coating failed completely while a sample embodying my invention only failed over a few local areas.

I have also discovered that the temperature can be lowered below 900° C., to effect a coating on the foundation metal. Samples were coated using a mixture composed approximately of 10% zinc and 90% chromium in one case, and approximately of 10% zinc, 5% aluminum and 85% chromium in another case. The coating process was carried out as described heretofore, the firing taking place in an ordinary electric resistor furnace for about four hours and the temperature being kept at about 700° C. The samples were analyzed after being coated, and the one coated with 10% zinc and 90% chromium mixture showed a chromium content in the coating of 2.36% and a zinc content of 79.64%, while the sample which was coated using the mixture containing 5% aluminum showed an analysis in the coating of 13.45% chromium, 62.16% zinc and 2.27% aluminum. This shows that it is possible to use a much lower temperature than 900° C., but that the chromium content in the coating is decreased. Such coatings will withstand ordinary rusting, but will not be as effective against oxidation at high temperatures as the metal coated at 900° C.

What I claim as new and desire to secure by Letters Patent of the United States, is:

1. The process of providing a foundation metal with a protective coating resistant to corrosion which consists in heating the foundation metal at a temperature in the approximate range 700° C. to 900° C. in the presence of a mixture of a coating metal and a metal which has a lower melting point than the coating metal and an affinity for the foundation metal.

2. The process of providing a foundation metal with a protective coating which consists in heating the foundation metal in contact with a mixture of zinc and a coating metal having a higher melting point than zinc, at a temperature sufficiently high to volatilize the zinc.

3. The process of providing a foundation metal with a protective coating resistant to corrosion and consisting mainly of chromium, which consists in heating the foundation metal at about 900° C. in the presence of a mixture of chromium and a metal which has a lower melting point than chromium and an affinity for the foundation metal.

4. The process of providing a foundation metal with a protective coating consisting

mainly of chromium, which consists in heating the foundation metal in contact with a mixture of chromium powder and zinc at a temperature sufficiently high to volatilize the zinc.

5 The process of providing a foundation metal with a protective coating consisting mainly of chromium, which consists in heating the foundation metal in contact with a mixture of chromium powder, zinc, and aluminum at about 900° C.

6 The process of providing a foundation metal with a protective coating consisting mainly of chromium, which consists in heating the foundation metal in contact with a mixture composed by weight substantially of 10% zinc, 5% aluminum, and 85% chromium having an iron content of about 1.5%, to a temperature sufficiently high to volatilize the zinc.

7 The process of providing a foundation metal with a protective coating consisting mainly of aluminum, which consists in heating the foundation metal, in contact with a mixture of aluminum, zinc, and alumina, at about 1000° C., the amount of zinc in the mixture being about 5% by weight.

8 The process of providing a foundation metal with a protective coating consisting mainly of aluminum, which consists in heating the foundation metal in contact with a mixture comprising 15 to 20% aluminum by weight, 1 to 5% zinc by weight, and 84 to 75% alumina by weight, at about 1000° C.

9 The process of providing a foundation metal with a protective coating consisting mainly of aluminum, which consists in heating the foundation metal in contact with a mixture comprising 20 to 40% aluminum by weight, 3 to 10% zinc oxide by weight, 77 to 50% alumina by weight, at about 1000° C.

10 The process of providing a foundation metal with a protective coating consisting mainly of aluminum, which consists in heating the foundation metal in contact with a mixture comprising about 30% aluminum by weight, about 5% zinc oxide by weight, and about 65% aluminum oxide by weight, at about 1000° C. in an atmosphere of hydrogen.

11 The process of providing a foundation metal with a protective coating which comprises heating the foundation metal in contact with a mixture of a coating metal and a metal which has a lower melting point than the coating metal and an affinity for the foundation metal, the temperature at which the heating is carried out being below 1000° C. but sufficiently high to volatilize the metal which is used in conjunction with the coating metal.

In witness whereof, I have hereunto set my hand this 27th day of May, 1929.

GOODWIN H. HOWE.