March 30, 1926. 1,578,254

I. T. BENNETT

PROTECTION OF METALS AGAINST CORROSION

Filed June 26, 1924

Fig. 1.

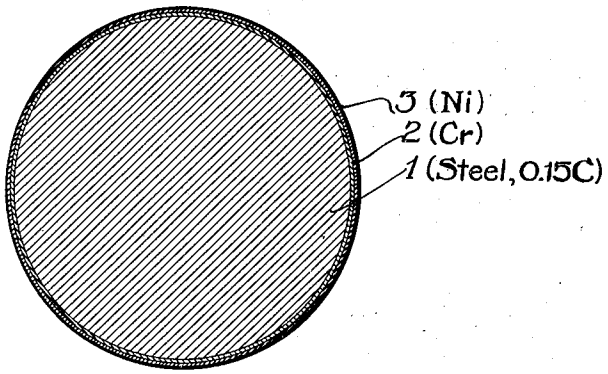


Fig. 2.

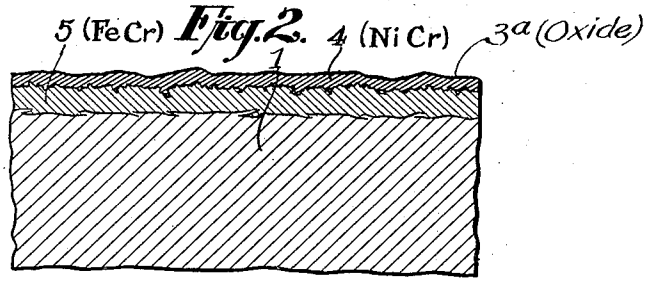
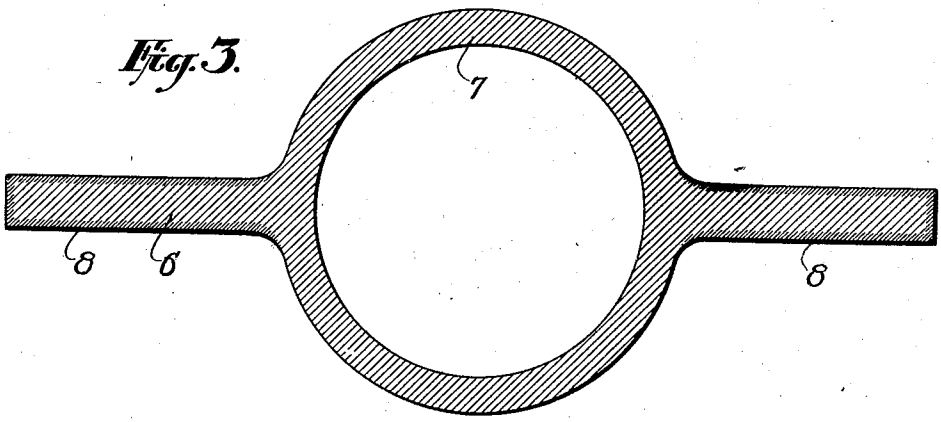


Fig. 3.



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UNITED STATES PATENT OFFICE.

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PROTECTION OF METALS AGAINST CORROSION.

Application filed June 26, 1924. Serial No. 722,462.

To all whom it may concern:

Be it known that I, IRVING T. BENNETT, a citizen of the United States, and a resident of Brooklyn, county of Kings, and State of New York, have invented certain new and useful Improvements in the Protection of Metals Against Corrosion, of which the following is a specification.

When steel and other metals are subjected to high temperatures they tend to oxidize more rapidly than at ordinary atmospheric temperatures. Various methods have been devised for treating steel to increase its durability under such conditions. The most successful of such methods have involved the formation upon the surface of the steel of a continuous, adherent film of oxide, which is non-porous and of low oxygen solubility. This film thus protects the underlying metal from further oxidation.

In practice I have found that the best of the known methods is effective only at moderately high temperatures, and that at exceedingly high temperatures the surface protection is not durable. My present invention aims to provide a surface which shall be durable at exceedingly high temperatures and which can be economically applied to steel, or iron, or similar metals; such as, for example, low carbon steel. I have demonstrated its success particularly with boiler tubes made of steel containing 0.15 to 0.20 per cent carbon. The invention is of particular value in connection with tubes provided with fins, as described in application No. 715,369, and other applications, of Thomas E. Murray. These tubes have longitudinal fins welded on to them and are in some cases located in the boiler furnace and exposed to the radiant heat of the burning fuel, so that they may be heated to an exceedingly high temperature, approaching 2500 degrees F. By treating such fins in accordance with the present invention, their durability under such conditions is greatly increased.

The articles of steel protected by the process are adapted also to various other uses, having a surface which is practically non-corrodible under ordinary conditions. The treatment may, in fact, be so applied as to make the articles practically insoluble in all acids, except for very slow solubility in aqua regia and hydrochloric acid. The accompanying drawings illustrate an embodiment of the invention.

Fig. 1 is a cross-section of a round rod illustrating diagrammatically the application of this invention to it;

Fig. 2 is a diagram taken from a photomicrograph of a section of such a rod;

Fig. 3 is a cross-section of a boiler tube with fins protected in accordance with the invention.

In the example of the invention illustrated, a steel rod 1, containing about 0.15% of carbon, is electroplated to form a coating of chromium 2. The rod thus produced is then electroplated to provide a second coating 3 of nickel.

The article, with these coatings deposited thereon, is then heated for two hours or more to a temperature in the range 1800 degrees F. to 2500 degrees F. in an oxidizing atmosphere. In this heating operation there are formed apparently alloys as indicated in Fig. 2. The outer surface is covered by a very thin continuous film of extremely adherent oxide indicated by the heavy line 3^a, which has practically the same coefficient of expansion as steel, and which is very dense or non-porous. This is probably a mixture of nickel oxide and chromium oxide intimately dispersed and of low oxygen solubility. Immediately below this is the coating 4, in all probability an alloy composed chiefly of nickel and chromium, in solid solution, which adheres closely to an inner coating 5 probably composed chiefly of iron and chromium in solid solution; which in turn adheres closely to the steel 1.

After heating it will be noted that there are two different layers. But these are not of the same composition as before heating. The outer layer 4 has a high resistance to acids and to extensive oxidation; whence, and from its appearance, I conclude that it is an alloy of nickel and chromium in solid solution similar to known alloys of these two metals.

The inner coating 5 merges into the steel in an ill-defined line. In some places the microscope indicates the formation of pearlite between this inner coating and the steel foundation. The coating 5 is apparently an alloy composed chiefly of iron and chromium in solid solution, being hard to etch and resistant to corrosion. Chromium

in this inner coating is also indicated by the formation of pearlite referred to, it being known that chromium lowers the eutectoid composition and permits the formation of more pearlite than in the case of ordinary carbon steels of a similar carbon content.

Chromium and iron alloy in the solid state when heated together under proper conditions of contact and atmosphere. But unless the conditions are reducing, the chromium oxidizes and union with iron does not take place. In my process the outer layer of nickel protects the chromium from oxidation during the heating operation and gives it a chance to penetrate the steel and alloy with it. At the same time the chromium alloys with the nickel to form a heat-resistant alloy which together with the thin film of adherent oxide aforementioned further protects the chromium iron alloy, which directly protects the steel. It is probable that migration of the chromium and nickel into each other is more rapid than the migration of the chromium and iron into each other. Thus the chromium coating is promptly protected and time is given for the formation of the iron chromium alloy.

The steel with the chromium and the nickel coating deposited thereon may be considered the finished product, ready to be put into use where it will be subjected to high temperature. In that case the conditions of use will fix the coatings by the oxidizing and alloying effects which have been referred to.

Or the article coated with chromium and nickel may be heated to fix the coatings as described before it is put into use. In heating the coated articles it is preferable to use an oxidizing atmosphere for, as previously mentioned, the success of the process depends on the formation of a proper oxide coating together with alloying effects produced by the heating.

Chromium is preferred because it is highly resistant to heat and because it combines readily with iron to form highly non-corrosive alloys, some commonly known as stainless steel. Nickel is preferred for the outer coating because it readily combines with chromium to form highly resistant alloys. The invention may be applied, however, with other materials than chromium and nickel. Also, though I have found electroplating a convenient method of applying the metals, yet they may be applied in other known or suitable ways.

The process is not confined to a single coating of each metal. There may be several coats of each metal, the two being deposited alternately; and indeed other metals may be added.

As an example of the method of depositing the chromium, a bath used may be of the following composition:

Chromic acid, 200–250 grams; chromium sulphate, 4 grams; water, 1000 cc.; anode of chromium; cathode of steel; cathode current density per sq. ft., 100 amps.; solution E. M. F., 2–3 volts.

I have found that two hours in such a bath will give a satisfactory deposit, and that agitation will aid this deposition.

An example of the method of depositing the nickel involves the use of the following bath:

Boric acid, 15 gm.; nickel-ammonium sulphate, 75 gm.; ammonium chloride, 15 gm.; water, 1000 cc.; anode of nickel; cathode of chromium deposited on steel; cathode current density (amps. per sq. ft.), 2–3; solution E. M. F., 1.5 volts.

Two hours in this bath gives a satisfactory deposit.

In using a greater number of coatings I propose, after the first compound coating of chromium and nickel, to coat in succession with chromium, iron, chromium and nickel, repeating this series as desired; the purpose of the iron being to alloy with the chromium on either side of it so that the heated article will consist of several layers of the two different alloys. Though the above order of deposition of the various metals is preferred, any other order which gives satisfactory results may be used; that is, the nickel may be deposited on the iron and the chromium on the nickel with but slight difference in properties.

I have subjected test pieces made as above with a single coating of the chromium and nickel to temperatures of 1800 and 2200 degrees F. for two hours in an oxidizing atmosphere and found the article to maintain a good looking surface with oxidation to a depth of only about one ten-thousandth of an inch; whereas the same steel, untreated, subjected to the same test was oxidized to a depth of from three hundredths to seven hundredths of an inch and badly scaled. With a temperature of about 2500 degrees F. for half an hour ordinary steel was badly scaled. The same steel treated as above showed no oxidation, and in the case of steel treated by a well known commercial process the aluminum oxide coating was starting to break down and expose the underlying steel. I have subjected test pieces made as above with a single coating of the chromium and nickel to temperatures of 1800 to 2300 degrees F. for 576 hours in an oxidizing atmosphere and found the article to maintain a good looking surface with oxidation to a depth of only one ten-thousandth of an inch; whereas the same steel untreated subjected to the same test was entirely destroyed by oxidation, burning up completely. Articles coated with chromium

and nickel, as described offer no difficulty in welding, so that they are well adapted to be applied as fins 6 (Fig. 3) to a boiler tube 7; the protective coating being indicated on the exposed surface 8 of the fins. Another advantage in this connection is that the coating does not substantially interfere with the heat-conducting property of the article.

I have subjected test pieces also to acids to determine their resistance to corrosion by acid vapors or liquids, and have found the corrosion-resisting and acid-resisting properties of the coated steel to be very high. Taking a sample which had been electroplated as above described and then heated in an oxidizing atmosphere to cause the oxidizing and alloying action, I immersed it in various acids and compared the results with those obtained by similar tests on commercial acid-resisting metals, chromium, nickel and alloys of nickel and chromium and of chromium and iron. Steel treated in accordance with the invention and heated to 1832 degrees F. for two hours showed a resistance to corrosion equal to that of chromium in all acids except concentrated hydrochloric acid in which it far surpassed chromium, being practically insoluble while the chromium rapidly dissolved. In fact, the protective coating on the steel treated according to this invention may be made to approach platinum in resisting acids. This resistance is due, in all probability, chiefly to insolubility of the oxide film and, secondly, to the two alloys underlying this film which are in themselves very similar to commercial resistant alloys.

The corrosion resisting properties of the treated steel make it valuable in laboratories and workshops where strong acids are employed or where, because of the corrosive fumes present, it would be impossible to use untreated steel.

The invention may be applied also to the protection of a piece of metal made up for practically or substantially its entire thickness by this process; that is, starting with a small core and building up with successive coatings to the desired size. For example, the fins 8 of Fig. 3 might be made up throughout all or the greater part of their thickness of the successive coatings described above.

I have stated above my theory as to what takes place in the application of my process. And it seems clear that the process is dependent on the diffusion of metals in the solid state, resulting in the formation of alloys or series of alloys which are extremely resistant to oxidation and to acids. But such diffusion is dependent on the temperature applied and the length of time of its application, and the product may vary in this respect within a considerable range. Such a variation is to be expected also where the metals used are of different compositions. For example, I have referred to steel or iron or similar metals, which I may include in the term ferrous metals, and I have gotten satisfactory protective results with both cast iron and wrought iron. But I should expect the direct results of the treatment to be different for each of these base metals.

The invention contemplates not only the use of nickel but also the use in the same way of equivalent metals; that is, metals closely allied in their chemical and physical properties, belonging to the same chemical group and occupying similar places in Mendelejeff's periodic table.

Though I have described with great particularity of detail certain embodiments of my invention, it is not to be understood therefrom that the invention is restricted to the embodiments illustrated. Various modifications thereof may be made by those skilled in the art without departing from the invention as defined in the following claims.

What I claim is:

1. The method of protecting the surface of ferrous metal, which consists in applying chromium thereto and applying a protective layer over the chromium.

2. In the protecting of the surface of ferrous metal, the method which consists in applying chromium thereto and applying nickel over the chromium.

3. The method of protecting the surface of ferrous metal, which consists in applying chromium thereto and applying to the surface an adherent oxide coating.

4. The method of protecting the surface of ferrous metal, which consists in applying chromium thereto and applying a protective layer over the chromium, and heating the article to cause the alloying of the iron and chromium, and to form on the outside an adherent oxide coating.

5. The method of protecting the surface of ferrous metal, which consists in applying chromium thereto and applying nickel over the chromium, and heating the article to cause the alloying of the iron and chromium and of the chromium and nickel, and to form on the outside an adherent oxide coating.

6. The method of protecting the surface of ferrous metal, which consists in applying thereto electrolytically a coating of chromium, protecting the latter by an outer coating, and heating the article to cause the chromium to alloy with the iron, and to form on the outside an adherent oxide coating.

7. The method of protecting the surface of ferrous metal, which consists in applying thereto electrolytically a coating of chromium, applying an outer coating of nickel

to the chromium and heating the article to cause the chromium to alloy with the iron and the nickel to alloy with the chromium, and to form on the outside an adherent oxide coating.

8. In the producing of a composite piece of metal the process which consists in applying a coating of chromium to ferrous metal and a coating of nickel to the chromium.

9. The method of producing a composite piece of metal which consists in applying a coating of chromium to ferrous metals and a coating of nickel to the chromium and heating the same to cause an alloying of the iron and chromium and of the chromium and nickel and to cause the formation of an outside coating of adherent oxide.

10. The method of protecting the surface of ferrous metal which consists in applying thereto protective layers, one of chromium and another of nickel.

In witness whereof, I have hereunto signed my name.

IRVING T. BENNETT.