

UNITED STATES PATENT OFFICE.

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METHOD OF COATING METALS. FLUX THEREFOR, ETC.

No Drawing.

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To all whom it may concern:

Be it known that I, RICHARD STAACK, a citizen of the United States, residing at North Bergen, in the county of Hudson and State of New Jersey, have invented certain new and useful Improvements in Methods of Coating Metals, Flux Therefor, Etc., of which the following is a specification.

This invention relates to the covering of metals with a protective coat or envelope to prevent corrosion, as for instance to the covering of iron or steel with a coating of lead, in such manner as to form on the iron or other metal, a closely adherent and continuous envelope or coat, substantially free from pin holes or breaks, and one which will effectually prevent corrosion or oxidation and will preserve the metal from the effects of the atmosphere and other deteriorating influences.

The need of such a protective coat for metal has long been recognized, and many attempts have been made to produce the same, but as far as I am aware without success. The prior attempts to this end have been characterized by the cleaning of the metal by subjecting it to different kinds of cleaning operations, most frequently by means of acid pickling solutions, the application to the cleansed metal of a flux, and finally the immersion of the metal in a molten bath of the coating metal. These characteristic operations have been carried on under different conditions and with the use of different kinds of pickling solutions, fluxes, and metal baths, but to my knowledge no commercially satisfactory coating has ever been produced which has successfully resisted corrosion and has protected the metal from the effects of the deteriorating influences to which in practice it is exposed.

As a result of many experiments and operations carried out under practical conditions, I have discovered that by the treatment of the metal in a certain way and under certain conditions, and with the use of an improved flux, and of a metal bath of certain ingredients, I am enabled to apply to the metal a non-corrosive envelope or coat which is closely adherent to the metal, is continuous in structure, practically free from pin holes or breaks, and which affords

an effective preventive against corrosion or oxidation for an indefinite time.

My invention therefore consists of an improved method of treating metals to give them a protective non-corrosive coating; and also of the improved flux employed in carrying out the method; and the method of treating coating baths to incorporate phosphorus therein.

In the specification to follow I shall point out and describe the details of my improved method, the materials used in carrying out the same, and the results thereof; and in the appended claims I shall set forth the novel characteristics and features of the invention.

In the use of my invention, in applying a protective coating of lead to iron or steel for instance, the preferred method of procedure is as follows:

The metal to be coated is first thoroughly cleansed of scale, oil, grease and other foreign substances. This cleansing may be effected in various ways now known to those skilled in the art, but I have found that the most satisfactory results are obtained if the article is first heated to redness, preferably a dull red, or say to a temperature of from 1100° to 1200° F. depending upon the thickness and size of the article, and then quenched in a suitable pickling solution. This heating of the article is preferably and conveniently effected by means of a heating flame playing upon it, the purpose of the heating being two-fold,—first, to consume or drive off the oil and grease, etc., and second, to open the pores of the metal in order that the ensuing action of the pickling solution may be more efficacious.

A pickling solution or bath which I have found to be satisfactory for the purpose, consists of a 5% to 7% solution of hydrochloric acid maintained at a temperature of from about 110° to 140° F. The article is kept in this solution for about three minutes more or less according to the nature of the article. After removal of the article from the pickling solution, it is washed in water so as to free it of the acid. Under certain conditions it may be desirable to use lower temperatures in the preliminary heating of the article, and this may be done if the duration of immersion in the pickling solution

be increased. I have found that the articles to be coated are sometimes in such condition as to require treatment preliminary to the above heating and pickling, such as a pickle
5 in dilute hydrofluoric acid, e. g. 15% strength.

The cleansed article has next applied to it a flux, which is conveniently effected by plunging the article in a bath of flux solution and allowing it to remain there for a
10 sufficient time to become thoroughly covered with the solution and for the latter to penetrate the pores of the metal. The treatment of the article by the particular flux
15 solution I employ, constitutes a very important step in the process, and in connection with the subsequent application of the molten coating material, it facilitates and aids in the close union of the coating material
20 with, and its adherence to, the metal of the article. The fluxing material which I employ for this purpose is a chloride solution, preferably chloride of zinc, containing phosphorus, such as is made by dissolving
25 metallic zinc in hydrochloric acid of about 20% commercial strength until the acid is nearly spent. This solution is diluted by the addition of water in sufficient quantity to leave in the solution a slight
30 excess of acid, and to it is added a suitable quantity of phosphorus, say 2 ounces of phosphorus to 20 gallons of the solution. The addition of the phosphorus to the solution may be conveniently effected by the use
35 of so-called "match sulphur" technically known as "phosphorus-sesqui-sulfide" or "tetra-phosphorus-tri-sulfide," which usually contains about 43 to 44% of sulphur and 56 to 57% of phosphorus. This "match sulphur"
40 is in lump form and the quantity added contains a greater amount of phosphorus than the solution will dissolve, my intent being to introduce and maintain a maximum of phosphorus in the flux. On
45 the addition of the match sulphur, the phosphorus is liberated from the sulphur and absorbed in the flux solution.

I have found that the immersion of the article for 30 seconds in the flux bath under the described conditions is sufficient for my
50 purposes.

While I prefer to add the phosphorus to the chloride solution by the use of so-called "match sulphur" as above described, it will
55 be understood that it may be introduced in other ways.

On removal of the article from the fluxing bath, and preferably while still wet with the flux solution, it is immersed in a metal coating bath. This coating bath is composed
60 mainly of lead in molten condition, with which is mixed a comparatively small quantity of phosphorus, and should be at a temperature of from 740° to 750° F. In one
65 form of my invention, the bath is made by

melting ninety-seven pounds of pure lead and adding to it three pounds of phosphor-tin. The immersion of the article in this bath should be effected slowly so as to prevent sputtering, and it should remain there-
70 in long enough to attain the temperature of the bath, one half minute or more, depending upon the size and thickness of the article.

On the removal of the article from the
75 metal coating bath, if it be a large article, it may be simply laid aside and the coating allowed to chill and set; but where smaller articles are coated, they are preferably agitated after removal from the coating bath
80 to prevent them from adhering to each other, and then may be dropped into kerosene or other quenching medium to cool them.

In order to give the article a thicker coating than would be applied by a single im-
85 mersion as described, it may be immersed in a second bath of coating metal,—in other words, subjected to the so-called "double dip." This may be effected by immersing the article, after the primary coat has set, in a
90 second bath having preferably a lower temperature than the first bath, say from 600° to 650° F. according to the melting point of the second bath. This second bath may be similar in its ingredients to the first bath,
95 or it may be free from tin and phosphorus and may contain a relatively small amount of antimony or other metal, say from 5% to 15%, which will have the effect of lowering the melting point of the bath. This will
100 give a harder and thicker second coat to the article. It may be desirable to quench the article between the two immersions, with a pickling solution, or with a flux solution, to render the surface thoroughly receptive to
105 the coating metal.

While I may introduce the phosphorus into the metal coating bath by the use of phosphor-tin as described, it will be understood that it may be added in other ways,
110 as for instance in the form of any phosphide or compound containing phosphorus.

By employing a chloride flux solution containing phosphorus, followed by a metal coating bath also containing phosphorus, in
115 the treatment of the article to be coated as above described, not only is the metal of the article made highly receptive to the close adhesion thereto of the metal of the coating bath, but also the latter is in the most
120 favorable condition to bring about a close and effective adherence of the coating metal to the article. The presence of the phosphorus both in the fluxing solution and in the coating bath, acts chemically I believe
125 to form on the surface of the article, to a greater or less extent, a phosphide or phosphides of iron, which constitute an intimate bond of adhesion between the lead of the bath and the iron of the article, and thereby
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results in a very effective coating of the lead, continuous and pin-hole-free in character. The coating therefore considered as an entirety is of a stratified character, consisting first of an underlying stratum of iron phosphide or phosphides immediately on the surface of the article, and a stratum of lead and phosphorus superimposed on the first stratum; and if the article is subjected to a subsequent dip or dips, as described, additional strata will be imposed on those first laid, such additional strata containing antimony or other metals, according to the particular ingredients of the additional baths.

The phosphorus in the coating bath has also a de-gasifying and de-oxidizing effect on the metal bath and surface of the iron article, and results in a more continuous coating than would be the case if oxids and gases were present, as these would cause holes in the coating, and a less perfect bond between the coating metal and the metal of the article.

The action of the lead in adhering to the article is facilitated by a certain amount of hydrostatic pressure exerted by the bath on the immersed article, which pressure may have the effect of forcing the lead into the pores and interstices of the metal. The osmotic pressure between the bath and the article coated also acts to the same end.

In the practice of my process under practical conditions, I have found it desirable to add phosphorus to the molten coating bath from time to time, in order to prevent the phosphorus content from being reduced to an undue degree or from being entirely exhausted by the continued use of the bath. Apparently but a very small percentage of the phosphorus content in a given amount of phosphor-tin, is absorbed by the lead of the bath, the remainder and greater portion of the phosphorus released by the tin when the latter melts, escaping or passing into the dross. A portion of this small phosphorus content forms, with the lead of the bath, phosphide of lead, and the remaining portion combines with the iron of the immersed article and forms phosphide of iron, so that unless the supply of phosphorus is kept up, there will be a constant loss, in the continued use of the bath on successive articles. By adding phosphorus from time to time as above described, the proper content is maintained in the continued use of the bath, and there will always be present a sufficient amount to combine with the iron of the article in forming the phosphide of iron stratum thereon.

While I have in the foregoing description set forth my invention as applicable by way of example to the coating of iron or steel with lead the invention may be applied to the coating of brass, bronze, copper and like metals with lead, in which case I have found

it advisable to employ as the pickling solution, a mixture of nitric and sulphuric acids, in which the article should be immersed for a moment only. This solution is in the proportions of 30% of nitric acid to 70% of sulphuric acid.

In using the method in the field, where pickling solutions and bath tanks are impracticable, and when erected structures such as steel bridges, steel building frameworks, and the like, are to be coated, the metal is cleaned by sand blasting, then the protective metal containing phosphorus and previously ground to a fine powder is mixed with the chloride flux solution to the consistency of metallic paint, and is applied to the metal structure to drench the same, and the wet composition is subjected to the action of direct heat which may be applied by means of a blow torch or otherwise, in order to reduce the protective metal to a molten state.

Having thus described my invention, what I claim is:

1. The method of covering metal with a protective metal coating, which consists in cleansing the metal to be coated, drenching the cleansed metal with a flux containing phosphorus, and uniting with the drenched metal a protective metal in molten condition containing phosphorus.

2. The method of covering metal with a protective metal coating, which consists in cleansing the metal to be coated, applying thereto a flux containing phosphorus, and immersing the flux covered metal in a bath of molten protective metal containing phosphorus.

3. The method of coating metal with lead, which consists in cleansing the metal, applying thereto a flux containing phosphorus, and finally immersing the metal in a bath of molten lead containing phosphorus.

4. The method of coating metal with lead, which consists in cleansing the metal, applying thereto a flux containing phosphorus in solution, and while the metal is still wet with the flux solution, immersing the same in a bath of molten lead containing phosphorus.

5. The method of coating metal with a protective metal covering, which consists in cleansing the metal to be coated, applying thereto a chloride flux containing phosphorus, and immersing the flux covered metal in a bath of molten protective metal.

6. The method of coating metal with a protective lead covering, which consists in cleansing the metal, applying thereto a chloride flux containing phosphorus, and immersing the metal in a bath of molten lead containing phosphorus.

7. The method of coating metal with a protective lead covering, which consists in cleansing the metal, applying thereto a chloride flux containing phosphorus, and im-

mersing the metal in a bath of molten lead.

8. The method of covering metal with a protective lead coating, which consists in cleansing the metal, applying thereto a chloride of zinc flux containing phosphorus, and immersing the metal in a bath of molten lead containing phosphorus.

9. The method of covering metal with a protective lead coating, which consists in cleansing the metal, applying thereto a suitable flux, immersing the metal in a bath of molten lead to give it a primary coating, allowing said coating to set, and immersing the coated metal in a molten lead bath of lower temperature than the first bath to give the metal a second coating.

10. The method of covering metal with a protective metal coating, which consists in cleansing the metal to be coated, applying thereto a suitable flux, immersing the metal in a bath of molten lead to give it a primary coating, allowing said coating to set, subjecting said coated metal to a treatment to make it receptive to a second lead covering, and immersing the metal in a bath of molten lead to give it a second coating.

11. The method of covering metal with a protective lead coating, which consists in cleansing the metal, applying thereto a flux consisting of a solution of chloride of zinc containing phosphorus in the proportion of two ounces of phosphorus to twenty gallons of the solution, and immersing the metal in a bath of molten lead containing phosphorus.

12. The method of covering metal with a protective lead coating, which consists in cleansing the metal, applying thereto a chloride flux containing phosphorus-sesqui-sulfide, and immersing the metal in a molten lead bath.

13. The method of covering metal with a protective lead coating, which consists in cleansing the metal, applying thereto a chloride flux containing phosphorus-sesqui-sulfide, and immersing the metal in a molten lead bath containing phosphorus.

14. The method of covering metal with a protective lead coating, which consists in heating the metal to redness, applying thereto while the metal is in heated condition, an acid pickling solution, freeing the metal of the pickling solution, applying to the metal a chloride flux solution containing phosphorus, and immersing the metal while still wet with the flux solution, in a molten lead bath containing phosphorus.

15. A flux for use in covering metal with a protective metal coating, consisting of

a chloride flux solution containing phosphorus.

16. A flux for use in covering metal with a protective metal coating, consisting of a solution of chloride of zinc containing phosphorus.

17. A flux for use in covering metal with a protective metal coating, consisting of a dilute solution of chloride of zinc containing phosphorus.

18. A flux for use in covering metal with a protective metal coating, consisting of a chloride flux solution containing phosphorus-sesqui-sulfide.

19. A flux for use in covering metal with a protective metal coating, consisting of a solution of chloride of zinc containing phosphorus-sesqui-sulfide.

20. A flux for use in covering metal with a protective metal coating, consisting of a dilute solution of chloride of zinc containing an amount of phosphorus in the proportions of two ounces of phosphorus to twenty gallons of the solution.

21. The method of covering metal with a protective coating, which consists in cleansing the metal, applying thereto a suitable flux, immersing the flux covered metal in a bath of molten protective metal containing phosphorus, and adding phosphorus to the coating bath from time to time to maintain its proper phosphorus content.

22. The method of covering ferrous metal with a protective lead coating, which consists in cleansing the metal, applying thereto a suitable flux, immersing the flux covered metal in a molten lead bath containing phosphorus, and adding phosphorus to the bath from time to time to maintain its proper phosphorus content.

23. The method of treating a molten metal coating bath to incorporate phosphorus therein, which consists in fusing phosphor-tin in the bath.

24. The method of treating a molten lead coating bath to incorporate phosphorus therein, which consists in fusing phosphor-tin in the bath.

25. The method of treating a molten lead coating bath to incorporate phosphorus therein, which consists in fusing phosphor-tin in the bath in the proportions of substantially 3 pounds of phosphor-tin and 97 pounds of lead.

In testimony whereof, I have affixed my signature hereto.

RICHARD STAACK.