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IRON-CONTAINING BASE COATED WITH NICKEL-PHOSPHORUS ALLOY

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Fig. 1

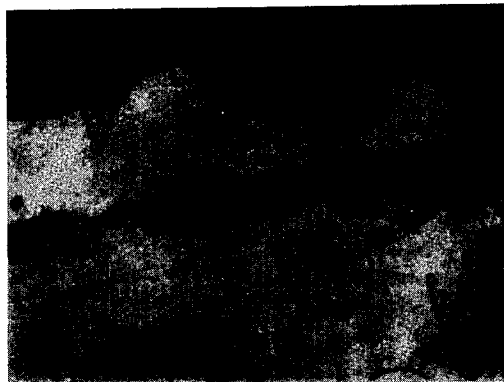
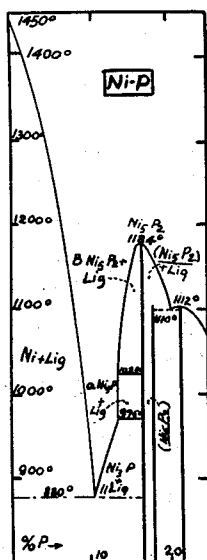


Fig. 2



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UNITED STATES PATENT OFFICE

2,633,631

IRON-CONTAINING BASE COATED WITH
NICKEL-PHOSPHORUS ALLOYGerald J. Horvitz, Woodmere, N. Y., assignor of
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Application October 4, 1948, Serial No. 52,612

1 Claim. (Cl. 29—196.1)

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My invention relates to a new and improved method of forming a corrosion-resistant alloy surfacing or coating on ferrous and non-ferrous metals, and on bodies made of other materials. The surfaces of said bodies on which the alloy surface layer is formed, is preferably non-porous and non-vitrified.

The bodies which are thus surfaced or coated may be tubes or plates or they may have any desired shape.

Coated tubes or bodies of this type may be used in stills, and more particularly in the stills which are used for cracking oil. The improved method and the improved coating may also be used for various other purposes, such as making coated resistors, grid leaks, emission coatings in vacuum tubes, and for other electrical purposes.

Another object of the invention is to provide an alloy coating which will be also interalloyed with the base metallic material. This base metallic material may be low carbon steel which may contain from 0.10% to 0.30% of carbon and less than 0.60% of manganese. However, the invention is not limited to the use of any particular type of steel or alloy or metal as the base material; such as, for example, wrought or cast, plain carbon steel or ferrous alloys, grey cast iron, malleable iron and "Monel" metal.

It is extremely important that the surface to be coated be absolutely clean. It should be absolutely free of rust, grease, dirt, scale, oil, paint or the like.

Other objects of the invention will be stated in the annexed description and drawings, which illustrate several embodiments of the invention.

Fig. 1 is a microphotograph, enlarged to a scale of 400 diameters and showing the improved coating applied to a base of low carbon steel.

Fig. 2 is an equilibrium diagram for nickel and phosphorus, showing the steep drop in the fusion point of this alloy, as the percentage of phosphorus increases up to 10%.

The base may be rigid or bendable. The improved coating is ductile, so that the coating can withstand bending, when it is applied to a thin sheet of steel of the type which is used for making cans for packing food products and the like.

Various methods have heretofore been used for applying anti-corrosion metal coatings. These methods have included electro-deposition, by de-

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positing metals having a relatively high melting point, such as nickel, or by depositing metals having a relatively low melting point, such as cadmium. It also has been well-known to dip the body to be coated in a molten bath of a metal or alloy having a relatively low melting point, such as a bath of lead, zinc, tin, cadmium, and in baths of various alloys of these low-melting metals. It has also been proposed to spray metals having relatively high melting points upon the bodies to be protected against corrosion.

Many of these methods are difficult to utilize in coating the interior surfaces of long pipes, heaters, and other bodies which have relatively small openings.

According to my invention, I apply to the surface which is to be coated, which may be an interior surface or an exterior surface of a body, a metallic oxide or oxides, or a metallic salt or salts, or a mixture of the same, together with a salt or salts, or an oxide or oxides, or an acid or acids, of certain selected elements of the fifth group. These selected elements of the fifth group have relatively low melting points and they consist of phosphorus, arsenic, antimony and bismuth.

The melting points of these selected elements are as follows:

Name of Element	Melting Point, ° C.
Phosphorus.....	44.1
Arsenic.....	814
Antimony.....	630
Bismuth.....	268

The major ingredient of the improved alloy coating is a metal which has a higher melting point than the aforesaid elements of the fifth group. Said major ingredient may be nickel, which has a melting point of 1450° C.; cobalt, which has a melting point of 1467° C., or copper, which has a melting point of 1083° C.

The invention is not limited to the use of the high-melting metals above mentioned, as these are stated only for purposes of illustration.

If a phosphorus compound is used under the conditions stated herein, some of the phosphorus

reacts with the hydrogen to produce phosphine, a part of which is driven off. Hence the percentage of phosphorus in the final alloy coating is less than the percentage of phosphorus in the mixture which is initially applied to the surface of the body. Similarly, arsenic and antimony and bismuth respectively combine with hydrogen, under the conditions stated, to form the corresponding gaseous hydrides, some of which are driven off.

As a preferred example of the invention, and without limiting the same to the ingredients or proportions or other details specified therein, the following is stated:

The mixture is made of nickelous oxide or nickel mono-oxide (NiO) and of ammonium dihydrogen orthophosphate in the ratio of $2\frac{1}{2}$ to 1, or 4 to 1, or 8 to 1. The nickel mono-oxide has a greenish black color and it is usually designated as the green oxide of nickel. The formula of the ammonium dihydrogen orthophosphate is $(\text{NH}_4)_2\text{H}_2\text{PO}_4$. This is also known as monoammonium phosphate. I can also use ammonium monohydrogen orthophosphate, whose formula is $(\text{NH}_4)_2\text{HPO}_4$. This is also known as diammonium phosphate. I can also use normal ammonium phosphate or triammonium phosphate, whose formula is $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$. I can also use nickel sesquioxide, whose formula is Ni_2O_3 , instead of the nickel mono-oxide. I can also use nickel carbonate (NiCO_3). The nickel sesquioxide has a grayish black color and it is usually designated as the black oxide. The above proportions may be varied, in accordance with the specific substances which are used to make said mixture.

The specific proportions above given are by weight and they relate particularly to mixtures of NiO and of $(\text{NH}_4)_2\text{H}_2\text{PO}_4$. Likewise, minor proportions of other ingredients may be added to the above mentioned mixture without departing from the invention. Cobalt oxide, when used without any other metal oxide, is not reduced satisfactorily when $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ is used under the temperature conditions stated above. However, when it is used to replace a part of the nickel oxide, satisfactory reduction is obtained. It can also be used under the conditions stated below. This cobalt oxide may be cobaltous oxide, whose formula is CoO , although I can use any of the various nickel oxides or cobalt oxides which can be reduced to the metallic state under the conditions later specified herein. These oxides may be used severally, or in mixtures. The percentage of cobalt oxide in the preferred example is preferably, but not necessarily, less than the percentage of nickel oxide. In the preferred example, the percentage of cobalt oxide may be about 3% of the percentage of nickel oxide.

This mixture is made with water or other liquid which is sufficient to produce a paint-like consistency so that when the mixture is brushed on the surface to be protected, a fairly thick coating will remain. The thickness of this coating may be 0.05 cm. The amount of water which must be added to the mixture, in order to produce a coherent and adherent coating will vary with the proportions which are used. In using the green oxide of nickel and $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ in the ratio of $2\frac{1}{2}$ to 1, I have found it sufficient to intermix 5 parts of said mixture with 1 to 2 parts of water. All the proportions stated herein are by weight. The mixture can be made in an ordinary machine which is used for mixing and grinding paints. The respective ammonium phosphates which are above mentioned, are freely soluble in water and

all or substantially all of the ammonium phosphate is dissolved in the water which is used in making the mixture.

The surface to be protected can be coated with this adherent mixture in any suitable manner, as by spraying, brushing, or the like.

The particle size of the water-insoluble ingredient of said mixture, such as the green oxide of nickel, may be about 1 to 5 microns.

The moist coating is then heated in a suitable reducing atmosphere which may consist of pure hydrogen or of other suitable gas or vapor or other reducing agent or agents, which can reduce the nickel oxide or the like to metallic nickel or the other respective metal. The reducing temperature may be from about 1600°F . to 1800°F . It is below the melting point of the metallic nickel or other high-melting ingredient or ingredients of the mixture. The coating may be dried at room temperature of about 70°F . before it is heated in the reducing atmosphere, but is preferred to heat and reduce the coating before it has lost any substantial part of its moisture. The action of the heated reducing agent decomposes the phosphate, and the phosphorus alloys with the nickel. Such alloys are also designated in the art as phosphides.

In the preferred example, hydrogen is used for the reducing gas. It is passed over the object at the rate of approximately 4 cubic feet per hour for each square foot of surface being treated.

An alloy coating of nickel and phosphorus is thus secured and this alloy is interalloyed to some extent with the base material, if this is a low carbon steel or other suitable metal or alloy. This alloy forms an impervious and adherent coating on a non-metallic surface. The invention is not limited to any particular method of reducing the aforesaid coating.

The line of junction between the coating and the base especially if this is made of low carbon steel, shows a complete or 100% bond with respect to porosity. This is essential in order to provide a strong and adherent and impervious and ductile and bendable coating.

In addition to using various ammonium salts which include phosphorus, I can use other salts or oxides of the selected fifth group elements, such as bismuth dioxide (Bi_2O_3), bismuth trioxide (Bi_2O_3), and other oxides of bismuth. I can also use the respective ammonium arsenates, such as ortho-ammonium dihydrogen arsenate, whose formula is $\text{NH}_4\text{H}_2\text{AsO}_4$. I can also use the ortho-ammonium monohydrogen arsenate, whose formula is $(\text{NH}_4)_2\text{HASO}_4$.

If copper oxide is used to replace all or part of the nickel oxide, a copper-phosphide coating is formed.

The reduction can take place at ordinary atmospheric pressure, or at a pressure which is above or below ordinary atmospheric pressure.

The invention generally includes the various oxides or salts or other compounds of the selected elements of the fifth group which are reduced or decomposed under the working conditions of the process, in order to yield the selected metal to form an alloy with the high-melting metal.

Under the conditions above mentioned, the alloy coating is preferably fused or it is at least sintered, in order to form a coherent and impervious coating, which preferably bonds the alloys coating with the metal of the base body. In the preferred example, the percentage of phosphorus in the phosphor nickel coating, in the early stages of the reduction is at least 8-10%,

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so that the melting point of the initially-formed eutectic alloy coating is approximately 1600° F. to 1838° F., or 880° C. to 1000° C. As reduction proceeds, the phosphorus content may be reduced to about 2% and the phosphor nickel has a melting point of 2400° F. or 1300° C. The improved coating is resistant to atmospheric corrosion, and it also offers satisfactory resistance to a hot solution of 5% sulphuric acid at a temperature of 180° F., and to a 1.20 solution of nitric acid in water, at ordinary room temperature of about 70° F.

Instead of using nickel or cobalt oxides or compounds, I can use the oxides or compounds of various other corrosion-resistant metals, whose melting points are higher than the melting points of the selected fifth group elements. For example, I can utilize a compound of chromium, which has a melting point of 1520° C., or a compound or molybdenum, which has a melting point of approximately 2620° C.

Of course the working temperature during the reduction may be varied, depending upon the melting or bonding point of the improved alloy, which will vary with the ingredients thereof. This working temperature is preferably, but not necessarily, less than the melting point of the base material. The invention is not necessarily limited to a coating which is either fused or sintered under the working conditions, but it is preferable that the working temperature should be high enough at least to sinter the coating, and preferably high enough to fuse the coating so as to interalloy the coating with the material of the base body, if this is made of metal. The melting of the coating is produced at relatively low temperatures, by combining or alloying the high-melting metal or metals with minor percentages of metals which have relatively low melting points, such as phosphorus, arsenic, antimony and bismuth. The invention is therefore not limited to the use of the elements of the fifth group which have been specifically designated.

The improved process and product can be used for replacing tinned plate, galvanized iron, a copper coating on iron or steel sheets or other bodies, for many purposes. It may be utilized for coating the tubes of condensers which are used for condensing steam, for coating pipes which are used for conveying acid or alkali materials, for coating metal ship plate in order to resist the corrosion of salt water, and for many other purposes.

Of course it has been known to make various alloys of copper and phosphorus, such as Phosphor bronze. These alloys consist of copper and tin and phosphorus in varying percentages. However, in ordinary Phosphor bronze there is merely a trace of phosphorus, as the percentage of phosphorus is usually not more than 0.15% to 0.2%.

According to the improved process, the alloy coating is formed in situ on the surface which is to be protected.

The invention generally covers the decomposition of any compound or compounds of one or more metals, while simultaneously decomposing a compound or compounds of another metal or metals of lower melting point than the first-mentioned metal or metals, thus producing an alloy which is formed in situ, said alloy having a lower melting point than the first-mentioned metal or metals.

As further examples of my invention, and in order to avoid limiting the same to any specific

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ingredients or proportions, the following examples are given of mixtures which produced good coatings, under the general working conditions above stated:

Materials	Proportion of Mixture
NiO+CoO+(NH ₄)H ₂ PO ₄	97:3:20
NiO+Bi ₂ O ₃ +(Water only).....	18:2:3
NiO+Bi ₂ O ₃ +(NH ₄ OH and water).....	18:2:3
CuO+Sb ₂ O ₃	10:1
Cr ₂ O ₃ wetted with a mixture consisting of equal parts of 1:1 HCl and H ₃ PO ₄ , which was used instead of water. The "NH ₄ OH and water" refers to chemically pure NH ₄ OH, with an ammonia content of 28%-39%.	
NiO+CoO+(NH ₄)H ₂ PO ₄	8:2:2.5
NiO+Cr ₂ O ₃ +(NH ₄)H ₂ PO ₄	4:1:1 or 8:1:1

Discontinuous and spotty coatings were also secured, under the conditions above mentioned, with the following:

Materials	Proportion of Mixture
CuO+Bi ₂ O ₃	4:1
CuO+NH ₄ H ₂ PO ₄	4:1
NiO+Sb ₂ O ₃	10:1
MnO+Sb ₂ O ₃	10:1
NiO+Sb ₂ O ₃ (wet with NH ₃).....	10:1
CuO+NiO+CoO+NH ₄ H ₂ PO ₄	2:6:2:2.5

The invention includes the formation of discontinuous and spotty coatings, as they are of value for some purposes.

Generally speaking, I form an alloy coating in situ on the surface of a body, by producing a coating of compounds of the metallic ingredients of said alloy upon said surface, and decomposing said compounds in situ and forming the alloy from said metallic ingredients in situ. This alloy coating may contain any suitable ingredients other than the major ingredients thereof. For the purposes of this specification, phosphorus may be considered as a metal, since in effect it forms an alloy with nickel, cobalt, copper and other metals. Ingredients other than phosphorus, which can be combined with metals to form material similar to alloys, can also be used instead of phosphorus.

The initial coating or surface layer which is formed upon the surface of the body, or on a part of said surface, may include a plurality of the compounds of elements which have the relatively low melting points, such as the selected elements of the fifth group. Likewise, said initial coating may include the compounds of a plurality of metals which have the higher melting points, such as nickel or cobalt or copper. Therefore, whenever I refer in the claim to the use, in said initial coating, of a compound of an element which has a relatively low melting point, I include the use of compounds of a plurality of said elements, and when I refer to the use, in said initial coating, of a compound of a metal which has a higher melting point, I include the use of compounds of a plurality of such metals.

Generally speaking, the metals whose melting points are approximately 658° C. or above may be designated as the high-melting metals. Whenever I refer to a coating in the claim, I include a continuous or discontinuous coating or surface layer, which may be applied to all or to part of the surface which is to be protected. The initial coating may be tightly or loosely adherent to the surface of the body or it may be confined to the surface of the body of a mold or in any other manner.

The compounds of the higher-melting metals, such as nickelous oxide or the like, are insoluble in water. The compounds of the lower-melting-point metals are soluble in water; and in making the coating mixture said compounds of the lower-melting-point metals are preferably wholly dissolved in the water. It would not be departing from the invention to use a liquid vehicle other than water. However, the invention is not restricted to this because I can use bismuth trioxide, which is substantially insoluble in water. The antimony oxides, such as antimony trioxide (Sb_2O_3), are insoluble in water.

I have stated numerous embodiments of my invention, in order to avoid being limited to any particular ingredients or proportions, but it is clear that numerous changes and omissions could be made without departing from the spirit of the invention.

The phosphor-nickel alloy above mentioned is the preferred embodiment, because it is closely similar to a nickel coating in color and lustre. The improved method can therefore be used for coating the inner and outer walls of food containers such as cans or the like, thus replacing the tin-plate which is now used.

If the surface which is to be coated is irregular, a wetting agent may be added to the initial mixture. In using the green oxide of nickel and ammonium dihydrogen ortho-phosphate in the ratio of $2\frac{1}{2}$ to 1, 5 parts of said mixture being intermixed with 1 part to 2 parts of water, as previously stated, the wetting agent is used in the proportion of 0.25% by weight. The preferred wetting agent is the dioctyl ester of sodium sulfosuccinate to the extent of 0.25%. The formula of the dioctyl ester of sodium sulfosuccinate is:

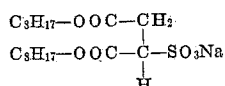


Fig. 1 is a cross-sectional view which illustrates the formation of a binary alloy of nickel and phosphorus upon a base metal of low carbon steel. The upper zone consists of a binary alloy of nickel and phosphorus. The darker crystals are higher in phosphorus and they appear to be of eutectic composition.

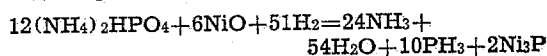
The zone of dark crystals which is located between the coating and the base metal consists of a ternary alloy of nickel, phosphorus and iron. The grain boundaries of the base metal have a tendency to fade out as the coating zones are approached. This results from some diffusion of nickel and phosphorus into the base metal.

The initial coating composition comprised a mixture of nickelous oxide and ammonium dihydrogen phosphate in the proportion of $2\frac{1}{2}$ to 1.

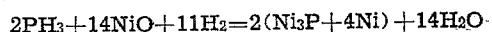
I can also use any of the phosphorus oxides in the initial coating, such as phosphorus trioxide (P_2O_3), phosphorus tetroxide (P_2O_4), or phosphorus pentoxide (phosphoric anhydride, P_2O_5) which are wetted either with water or with ammonium hydroxide. I can also use any of the

modifications of phosphoric acid, namely, ortho-phosphoric acid ((H_3PO_4) or $(\text{H}_3\text{PO}_4)_2\text{H}_2\text{O}$), pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$), or hypo-phosphoric acid ($\text{H}_2\text{P}_2\text{O}_4$).

While there are numerous intermediate reactions, the invention involves two main reactions, with respect to nickel, as follows:



and



In the first reaction the diammonium phosphate or the like reacts with the nickelous oxide and the hydrogen of the reducing atmosphere, to produce an alloy of nickel and phosphorus, which contains about 10% of phosphorus. As illustrated in Fig. 2, this is the eutectic alloy of nickel and phosphorus. The other products which result from said reaction are ammonia, and water vapor, and phosphine.

In the second reaction, the phosphine reacts with some of the nickelous oxide, to produce a mixture of nickel and a nickel-phosphorus alloy. This mixture of nickel and of nickel phosphorus alloy forms a protective coating in which the percentage of phosphorus in the total coating is less than 3%. These reactions require the use of an excess of nickelous oxide, in relation to the quantity of the diammonium phosphate or the like, in the ratio of 2.5 to 1, or 4 to 1, etc., as previously stated.

This application constitutes a refiling of my lapsed application Serial No. 355,283, filed September 4, 1940.

I claim:

A base body made of metal containing iron and having a surface coating which consists substantially of a binary alloy of nickel and phosphorus, the proportion of phosphorus being substantially two per cent, the inner face portion of said coating having a higher percentage of phosphorus than the outer face portion of said coating, said body and said surface coating have an intermediate zone which consists substantially of a ternary alloy of nickel and phosphorus and of the ferrous metal of said base body.

GERALD J. HORVITZ.

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