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[54] **PRODUCING PROTECTIVE COATINGS ON METAL**

[76] Inventor: **Joachim Marx**, Schwerinstr. 34-38, Muelheim, Ruhr-Styrum, Germany

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[58] **Field of Search** ..... 148/6.15 R, 6.15 Z

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Primary Examiner—Leon D. Rosdol
Assistant Examiner—Charles R. Wolfe, Jr.
Attorney, Agent, or Firm—Burgess, Dinklage & Sprung

[57] **ABSTRACT**

The process for the production of a protectively coated metal object which comprises applying to said metal object at least one condensable phosphate selected from the group consisting of alkali metal hydrogen phosphates and alkali metal ammonium phosphates and thereafter heating said object to a temperature above about 400°C whereby said phosphate undergoes condensation to produce a glass-like protective coating. The metal object, which may be bright or freshly surface-oxidized, is preferably iron or an iron alloy and the phosphate preferably is of the formula

$Me_nX_2P_nO_{(3n+1)}$

in which

each X is a hydrogen or ammonium ion,

n is an integer,

Me is an alkali metal ion which, when n is 4 or more, may be partially replaced by a hydrogen, ammonium or equivalent of a polyvalent metal ion.

11 Claims, No Drawings

PRODUCING PROTECTIVE COATINGS ON METAL

In the hot shaping of metals, especially iron and iron alloys, by forging or rolling, for example, an oxide coating forms on the still incandescent metal. This oxide or scale coating interferes with further processing, and therefore it is usually removed, the method and time of removal depending on the nature the products involved. In the case of semifinished products, shapes and girders, for example, the scale interferes with examination for cracks, and therefore it is removed by sand blasting; then rustproofing coatings or paints are applied to prevent the bright metal from oxidizing again. In order to diminish the high costs due to the loss of iron through the formation of scale and to diminish the amount of de-scaling made necessary thereby, it has already been proposed that the workpieces be deoxidized in the hot forming process by the application of boron, phosphorus or aluminum compounds and that a protective coating be applied prior to cooling. The protective coatings known hitherto for this purpose, however, do not meet the requirements, because at the temperatures of the hot forming processes of 900° to 1,250°C, they are not sufficiently temperature-stable, or because the coatings formed by such means do not offer sufficient protection against rust, are poorly suited as foundations for lacquering, or for example do not have any electrical insulating properties.

Coatings on a phosphate basis for insulation and protection against corrosion are known. These are primarily coatings consisting of orthophosphates of the metals calcium, barium, magnesium, aluminum, zinc or manganese. In some cases the coatings are also formed by a reaction, by phosphoric acid for example, with the material to be treated, especially steel, and then they consist of orthophosphates of iron for example.

These coatings, however, are still porous as a rule, i.e., they require sealing, with insulating varnishes for example, and they are not strong enough for many purposes. Furthermore, their application requires additional process steps which are difficult to coordinate with the process of manufacturing sheet metal or wires. Steel strip is usually pickled to remove scale after it has been hot rolled from the bars, then cold-rolled to the final dimensions, and then annealed above 750°C to achieve the desired mechanical or electrical and mechanical properties. This is followed either at the mill or at the user's premises by the application of conventional rustproofing by washing, phosphatizing, washing, passivation and drying.

It is accordingly an object of the invention to provide a simple process whereby the formation of scale on metals in hot forming operations may be considerably reduced if not entirely eliminated, and at the same time high-quality, electrically insulating and anticorrosive coatings can be obtained on objects made of metals, especially iron and iron alloys.

These and other objects and advantages are realized in accordance with the present invention pursuant to which there is applied to the bright or surface-oxidized metal object an alkali metal hydrogen phosphate or an alkali metal ammonium phosphate which can be condensed to substantially neutral high-polymer phosphates (metaphosphate), and then heating the metal object to a temperature above about 400°C.

The condensable alkali metal phosphates may be represented by the formula

$Me_nX_2P_nO_{(3n+1)}$

in which

each X is a hydrogen or ammonium ion,

n is an integer,

Me is an alkali metal ion which, when n is 4 or more, may be partially replaced by a hydrogen, ammonium or equivalent of a polyvalent metal ion.

Examples of suitable alkali metal hydrogen phosphates wherein $n = 1$ to 3, which when heated to temperatures above about 400°C, especially about 600° to 1150°C, condense to alkali metal polyphosphates, are primary alkali metal phosphates, such as sodium dihydrogen phosphate ($NaH_2PO_4.H_2O$) and potassium dihydrogen phosphate ($KH_2PO_4.H_2O$), and alkali metal hydrogen pyrophosphates such as disodium dihydrogen pyrophosphate ($Na_2H_2P_2O_7$) and dipotassium dihydrogen pyrophosphate ($K_2H_2P_2O_7$). The use of corresponding lithium, rubidium or cesium hydrogen phosphates is possible, but offers no particular advantages.

Preferred for the purposes of the invention are water-soluble acid polyphosphates of the general formula

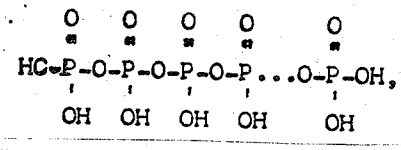
$Me_nH_2P_nO_{(3n+1)}$

in which

Me is an alkali metal, hydrogen, ammonium or equivalent of a polyvalent metal ion, and

n is 4 to about 100, especially 4 to about 15.

These acid polyphosphates and partially neutralized polyphosphoric acids are derived from commercial polyphosphoric acids of the general formula $H_{(n+2)}P_nO_{(3n+1)}$ and



respectively. The P_2O_5 content of these polyphosphoric acids increases with the average chain length. For the purposes of the invention, polyphosphoric acids are used as starting materials whose P_2O_5 content is greater than 83, preferably greater than 84%, by weight. In these polyphosphoric acids the tetraphosphoric acid content ($n = 4$) and the content of higher polyphosphoric acids is above 60%. In the case of a polyphosphoric acid with 84.2 wt-% P_2O_5 it already amounts to 74.2%. According to measurements by Rudy and Schloesser, Ber. d. dt. chem. Ges. 73, 484 (1940), only one hydrogen atom per phosphorus atom is strongly acidic. Accordingly, the average group in the chain bears only one hydrogen atom, a strongly acid one, and although the terminal groups bear two hydrogen atoms, only one of them is strongly acidic.

For the preparation of the acid polyphosphates to be used in accordance with the invention, the starting products may be those commercial polyphosphoric acids which contain mainly tetraphosphoric acid and higher polyphosphoric acids up to about n = 100 (Canadian Journal of Chemistry, Vol. 34, 1956, p. 790). The small amounts of ortho, pyro and triphosphoric acid or polyphosphoric acid with n greater than 100 which may also be present do no harm.

The said polyphosphoric acids are partially neutralized by the addition of the amount of alkali metal or ammonium hydroxide corresponding to the desired de-

gree of neutralization. Also, the acid polyphosphates to be used in accordance with the invention may be obtained by double decomposition of the polyphosphoric acids with salts of volatile acids, e.g., carbonates or acetates, of the metals that are to be introduced. All chemists are familiar with these methods. For the desired action it is essential that the acid polyphosphates still contain at least 2, preferably 3 or more, acid POH groups which are to be available for the further condensation or for the reaction with metal oxides, as the case may be. For the purposes of the invention, acid potassium and sodium polyphosphates are preferred, especially those which contain both potassium ions and sodium ions in the molecule. It is desirable for the molar ratio of potassium to sodium in the acid polyphosphates to be about 7 : 1 to 1 : 1, i.e., approximately ½ to ⅞ Me is replaced by K and from ½ to ⅛ Me is replaced by Na.

The use of acid lithium, rubidium or cesium polyphosphates or of acid polyphosphates containing several alkali metals is possible, but offers no particular advantage.

The properties of the protective coatings produced from the acid polyphosphates may be modified in the desired manner by the introduction of polyvalent metal ions, the polyvalent cations being, of course, bound to the polyphosphoric acid molecule by a number of oxygen atoms corresponding to their valency. Polyvalent ions which can thus serve to a certain extent, along with alkali metal or ammonium ions, for the partial neutralization of the polyphosphoric acids are, for example, Mg, Zn and Al. Desirably their equivalent in the acid polyphosphates should not exceed $n/2$.

The pH value of the acid polyphosphates is governed by the degree of neutralization. To prevent the acid polyphosphates from attacking the metal too violently it is recommendable to adjust the polyphosphoric acids with the said metals, i.e., especially the alkali metals, to a pH value of about 2.5 or more, although care must be taken to see that an average of at least two acid POH groups remain in the molecule. These acid groups are necessary to permit the acid polyphosphates to condense still further when they are heated so that substantially neutral high-polymer phosphates will form, with or without cross-linking. These will form a dense, glassy film, or a so-called phosphate glass. The acid polyphosphates used in accordance with the invention may thus also be considered as precisely adjusted precondensates for the preparation of highly polymerized phosphate glass coatings. A direct attack on the metal would prevent the additional condensation, so that the average chain length of the polyphosphates used would remain approximately the same, or in the event of further condensation a chain interruption would occur, which also would work against the formation of the highly polymeric phosphate glass. The reaction of the acid polyphosphates with metal oxides such as iron or titanium oxide would, on the other hand, contribute towards cross-linking and hence to the formation of phosphate glass if there is a sufficient number of acid groups in the polyphosphate molecules. Glass formation may be promoted by the addition of B_2O_3 or $Na_4B_2O_7$ and oxides of the Fourth Main Group and Sub-Group of the periodic system, such as SiO_2, PbO and TiO_2, for example, since such compounds are easily compatible with the phosphate glass. However, the quantity of these oxides which is added for the modification of the phosphate glass should not exceed about 20% of the weight of the acid polyphosphates.

For use with very sensitive metal alloys in which a premature reaction in the cold might be possible, the acid polyphosphates to be used according to the invention may be completely neutralized with ammonia, i.e., to a pH of about 8 to 9. From about 80°C up, ammonium polyphosphates yield ammonia and then again form acid polyphosphates which can further condense. The same is true of the alkali metal ammonium phosphates and alkali metal ammonium pyrophosphates which are obtainable by neutralization of alkali metal hydrogen phosphates and alkali metal ammonium phosphates with ammonia and which likewise may be further condensed when they are heated and yield ammonia. A condensation reaction then takes place with these compounds the same as it does with the alkali metal hydrogen phosphates in which $n = 1$ to 3, with the formation of more highly polymerized alkali metal metaphosphates or alkali metal polyphosphates, probably in the nature of Graham's or Kurrol's salts. This process may be represented as follows, based on the example of the primary sodium phosphate:

$$X\ NaH_2PO_4.H_2O \rightarrow X\ NaH_2PO_4 \rightarrow X/2\ NaH_2P_2O_7 \rightarrow (NaPO_3)_X$$

When these condensed phosphates form in the melt they also include any polymeric phosphates or other solids that may have been added. The simple or only slightly condensed alkali metal hydrogen phosphates are easily soluble in water, but yield solutions of relatively low viscosity which can drain off from perpendicular surfaces on the articles to be treated. Even so, if they are applied in a suitable manner, e.g., by spraying them onto objects heated above 100°C, or by evaporating the water immediately after application, after heating they can produce serviceable metaphosphate coatings in accordance with the invention.

If an alkali metal metaphosphate, especially potassium metaphosphate, is added to an aqueous solution of sodium phosphates condensable to metaphosphate, mixed, if desired, with potassium phosphates which are condensable to metaphosphate, viscous solutions are obtained which can more easily be applied in a uniform coat. Polymeric potassium metaphosphate $(K\ PO_3)_x$, x= about 400 to 20,000, also called potassium polyphosphate, swells and slowly hydrolyzes in aqueous solutions. Aqueous solutions or suspensions of mixtures of potassium polyphosphate and sodium dihydrogen phosphate in a weight ratio of about 1:2 to 1:2.5 and with a solid content of about 30 to 40 weight-percent, have also proven very useful.

Finely powdered inorganic solids which do not react with the primary alkali metal phosphates under the conditions of the heat treatment, such as mica or pigments, for example, may be incorporated in quantities of up to about 30%, preferably of about 3 to 10%, of the weight of the phosphate, and they increase the coating thickness.

The method of application depends in particular upon the process being used in working the metals with which they are used. For example, during or towards the end of the hot forming operation, e.g., rolling or forging, they can be applied to the surface of the incandescent-hot workpieces, so that right at this stage they can prevent oxygen corrosion (fire scale). In many cases it may be sufficient to provide the completely formed but still red-hot metal workpiece with a protec-

tive coating in accordance with the invention. In this high-temperature coating process the acid polyphosphates are best applied in the form of a dry powder which melts on the metal surface, reacts in the above-described manner within itself and in some cases with the oxides present on the metal surface, and forms the desired protective coating as a dense, glassy film.

The acid polyphosphates may thus be applied to the bright metal or to the superficially oxidized metal. The process of the invention is applicable to all metals whose oxygen corrosion is to be prevented or which are to be provided with a chemically resistant and/or insulating protective coating before they are further processed. It is preferentially intended for iron and ferrous metals and their alloys, e.g., nicken and chromium alloys, and for titanium, copper, and alloys thereof.

If chilling due to evaporation can be tolerated, or if substantially cold metal objects are to be provided with the coating of the invention prior to another working procedure, the coating is advantageously applied in the form of an aqueous solution, especially a 20 to 60% aqueous solution. This is done in any known manner, e.g., by immersion or spraying or by application with rubber rollers. The objects bearing the liquid coating are then placed in the annealing furnace either after drying or, if desired, directly into the annealing furnace if the steam which this produces is not excessive. The necessary application of heat is thus performed, preferably in the course of the annealing process customarily applied especially to sheets and wire. Since the high-molecular-weight polyphosphates are formed on the metal surface from the fused state, they are intimately bonded and tightly adherent to the metal surface. The desired effect is fully achieved at coating thicknesses of up to about 25 μm, and as a rule at thicknesses of as little as about 0.1 to 10 μm. The desired coating density can easily be achieved by appropriately controlling the quantities and concentrations of the coating material.

The duration of the required heating depends on the temperature. Whereas at 400°C approximately 1 minute is required for the formation of a glassy protective coating of the necessary quality, a few seconds will suffice at the preferred temperatures above 600°C. The reaction temperature also depends on whether just a phosphate glass only is to be formed on the metal surface, or whether oxides are to be included, such as Al_2O_3, Fe_3O_4, B_2O_3 or SiO_2.

The electrical resistance of the coatings of the invention amounts to about 5 to 1,000 ohms/cm², depending on their thickness, and thus corresponds to the resistance of comparable organic varnishes. The coatings of the invention are at the same time very practical primers for varnishing, lime coating or bonderizing, and good holders of lubricant in subsequent forming operations. They also offer the possibility of drawing wire directly without separate surface treatment. On the basis of the reaction whereby they are formed, the alkali metal metaphosphate coatings permit further heat treatments and prevent the formation of flaky fire scale. They do not interfere with the decarbonization which takes place in the final annealing.

By the addition of chromium oxides or powdered charcoal mixed with calcium carbonate certain effects of decarbonization of the edges of semifinished goods can be compensated, or the decarbonization can be favorably influenced, in the case of sheets for electrical industries, for example.

The protective coatings produced in accordance with the invention are nearly impermeable to gases. In the heat treatment of titanium under hydrogen, therefore, they prevent the absorption of hydrogen by the metal which is otherwise observed. It has been found that they are "weldable," i.e., they do not interfere with welding, especially the welding of objects of iron and ferrous alloys.

The invention is further described in the following illustrative examples wherein all parts are by weight unless otherwise expressed.

EXAMPLE 1

An aqueous solution of a polyphosphoric acid having a P_2O_5 content of 84.5% was neutralized to pH 2.5 with a KOH—NaOH solution in which the molar ratio of KOH to NaOH was 7 : 1, and the aqueous solution of this acid polyphosphate was adjusted to a content of 30% solids by weight. The solution was continuously applied by immersion to coil and to steel strip and heated in air in the annealing furnace to 450°C, whereupon a glassy film from 0.1 to 1.5 μm thick was formed, which showed good bending, stamping, cutting and deep-drawing strength. It easily replaces the phosphatizing that is commonly performed, for example, before the varnishing of auto body steels. The electrical resistance measured in accordance with DIN 50464 averages not lower than 25 ohms/cm² and has achieved values of up to 100 ohms/cm².

EXAMPLE 2

An aqueous solution of a polyphosphoric acid with a P_2O_5 content of 84% was neutralized with $Mg(OH)_2$ and then with KOH and NaOH up to a pH of 4.5. The acid polyphosphate solution, in which the atomic ratio of K : Na : Mg was 2.5 : 1.0 : 0.25, was adjusted to a content of 40% solids by weight and sprayed onto hot-rolled wire having a temperature of about 600°C, and dried as well as further condensed by the heat of the wire. The wire thus coated with a phosphate glass film can be cold-drawn without further treatment such as pickling or lime coating.

EXAMPLE 3

An aqueous solution of a polyphosphoric acid with a P_2O_5 content of 84% was neutralized to a pH of 2.5 with KOH—NaOH solution in which the molar ratio of KOH:NaOH was 1:1, and the aqueous solution of acid polyphosphate thus obtained was adjusted to a content of 50% solids by weight. This solution was continuously sprayed through ring nozzles onto slabs or girders which had just been rolled and had a temperature of 900° to 1,500°C. The phosphate glass film which condensed on them enables cracks to be seen easily after cooling. Without further treatment it serves as a primer for later varnishing and thus makes sandblasting unnecessary.

EXAMPLE 4

The aqueous, acid, sodium-potassium-polyphosphate solution prepared in accordance with Example 3 was evaporated to dryness on a heated drying cylinder, then ground to powder. The powder was applied to incandescent-hot semifinished pieces, whereupon the desired phosphate glass film was formed from the melt on the surface of the metal.

EXAMPLE 5

The solution of Example 3 was adjusted to a content of 40% solid matter by weight. It was used for coating castings and rolled products of titanium by dipping, and after brief drying was subjected to the customary annealing under inert gas containing hydrogen. As a result of the phosphate glass film that formed in accordance with the invention, the hydrogen absorption remained less than 100 mg/kg, so that the otherwise customary operations for the removal of the absorbed hydrogen were rendered unnecessary.

EXAMPLE 6

A mixture of
15 g monosodium dihydrogen phosphate
5 g commercial potassium metaphosphate and
20 g monopotassium [Monokalium] dihydrogen phosphate in
100 g of water

yielded a clear, viscous solution. This was applied to sheets for electrical industries with rubber rollers in a film 5 microns thick and then placed in the annealing furnace where the metal was heated for approximately 3 minutes at 750°C. The emerging band was uniformly covered with the protective coating and required no further treatment in this respect. The electrical resistance on scale-free surfaces with micro-roughnesses of about 3 microns was as follows, measured in accordance with the DIN proposed standard between two electrodes of 5 cm^2, a pressure p of 10 kp/cm^2 and a voltage of 100 mV DC:

Thickness microns	Approximate resistance ohms/cm^2
3	10
5	50
7	300
9	$9 \cdot 10^3$

It will be appreciated that the instant specification and examples are set forth by way of illustration and not limitation, and that various modifications and changes may be made without departing from the spirit and scope of the present invention.

What is claimed is:

1. The process for the production of a protectively coated metal object which comprises applying to said metal object a material consisting essentially of at least one condensable phosphate of the formula

$Me_nX_2P_nO_{(3n+1)}$

in which
each X is a hydrogen or ammonium ion,
n is from about 4 to 100,
Me is an alkali metal ion which may be partially replaced by a hydrogen, ammonium or equivalent of a polyvalent metal ion,

and thereafter heating said phosphate to a temperature of about 600° to 1150°C whereby it undergoes condensation to produce a glass-like protective coating.

2. The process of claim **1,** wherein said metal object comprises iron or an iron alloy.

3. The process of claim **1,** wherein said metal object has a temperature above about 400°C during application of said phosphate.

4. The process of claim **1,** in which X is hydrogen.

5. The process of claim **4,** in which *n* is 4 to about 15.

6. The process of claim **1,** in which Me is at least one of sodium and potassium.

7. The process of claim **6,** in which Me is sodium and potassium in the approximate molar ratio of K:Na = 7–1:1.

8. The process of claim **1,** in which at least one Me is hydrogen.

9. The process of claim **1,** wherein the condensable phosphate is an acid polyphosphate with a P_2O_5 content of at least about 83% by weight.

10. The process of claim **9,** wherein the acid polyphosphate is employed in aqueous solution which has been neutralized to a pH of at least about 2.5.

11. The process of claim **10,** wherein an alkali metal metaphosphate is added to the aqueous solution as a thickening agent.

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