United States Patent

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[72] Inventors **Masanaga Okabe;**
Kakuro Muro; Masamichi Iizuka; Sumio Sakata, all of Tokyo, Japan
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[73] Assignee **Hooker Chemical Corporation**
Niagara Falls, N.Y.
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[33] **Japan**
[31] **43/78918**

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[54] **PROCESS FOR PHOSPHATE CONVERSION COATING**
6 Claims, 2 Drawing Figs.

[52] **U.S. Cl.** .... **148/6.15 Z**
[51] **Int. Cl.** **C23f 7/08**
[50] **Field of Search** .... 148/6.15 R, 6.15 Z

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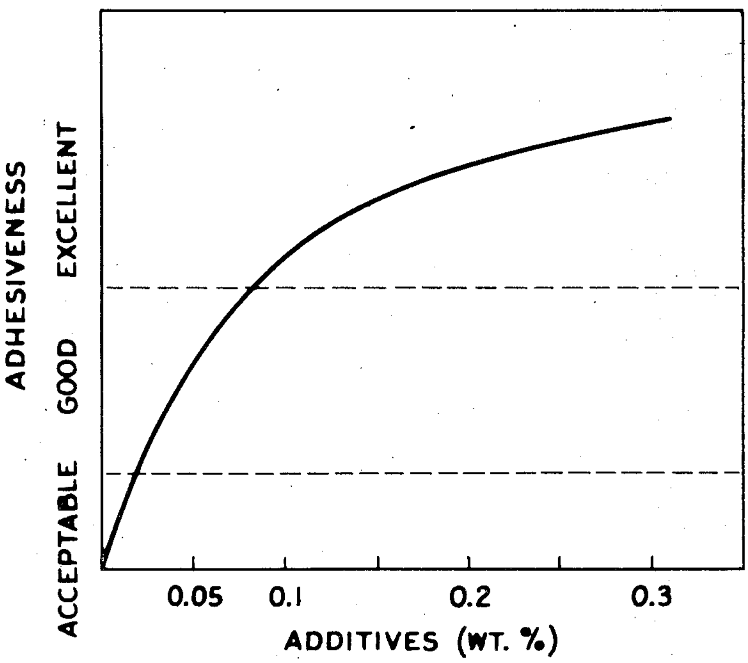
Primary Examiner—Ralph S. Kendall
Attorneys—Stanley H. Lieberstein and William J. Schramm

ABSTRACT: An improvement in the process of phosphate conversion coating on the surface of metals such as iron, steel, zinc or its alloy being characterized in that at least one carbohydrate selected from the group consisting of starch, starch derivatives and polysaccharides produced by acid decomposition of starch or starch derivatives, is added into ordinary acid zinc phosphate conversion coating solution, wherein a fine and dense zinc-phosphate-coating film can be obtained, and thereby improving paint bonding quality of the coating when the paint is applied to said coating and corrosion resistance of the coated metals.



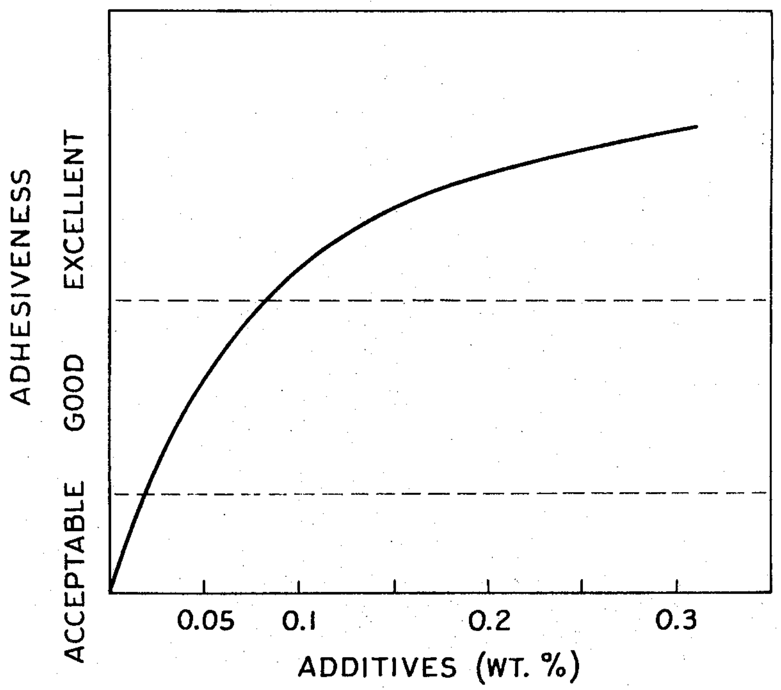

ADHESIVENESS
ACCEPTABLE
GOOD
EXCELLENT
0.05
0.1
0.2
0.3
ADDITIVES (WT. %)

Fig. 1

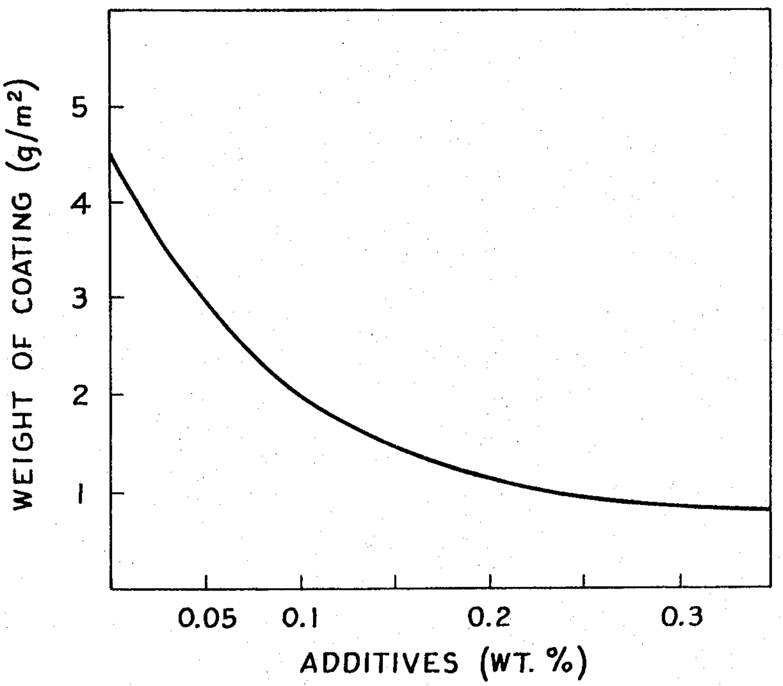

WEIGHT OF COATING (g/m²)
5
4
3
2
1
0.05
0.1
0.2
0.3
ADDITIVES (WT. %)

Fig. 2

PROCESS FOR PHOSPHATE CONVERSION COATING

This invention relates to improvements in process for phosphate conversion coating, that is, a method for forming coating films of zinc phosphate on surfaces of metals, particularly iron, steel, zinc and its alloys (including electrogalvanized and hot dip galvanized steel,) and is aimed to attain fine and dense crystalline structure of zinc phosphate of the coating, along with considerable reduction in weight (or in thickness) of said coating and increasing in adherence of the same to base metals, thereby to improve paint bonding quality of the coating when the paint is applied to said coating and corrosion resistance of the coated metals.

A particular object of this invention is to provide a method for the formation of strong zinc phosphate coating which can withstand bending up to 180° or other severe mechanical forming operation without failing such as falling off, cracks or other ruptures.

This invention is available in very wide range as far as the acid zinc phosphate coating concerns, and is able to get similarly good results irrespective of kinds of metals to be coated, and in turn, irrespective of composition of ordinary treating solution to be used. Accordingly, with any of iron, steel, zinc or zinc alloys the above-mentioned objects are easily attained by the method of this invention, and these wide versatility constitutes an important special feature of this invention.

Recently, consumption of so-called precoated metal or colored steel is becoming enormous. However, when such metals are subjected to severe mechanical forming operation such as 180° bending, cramping, etc. in practical use, it is rather usual that there occurs cracking or falling-off of the paint film at bent parts, resulting in corrosion of such defective points, which leads to short life of such metals.

As well known, possibility of occurrence of defects such as cracking or falling off of the paint film is less in thinner chemical coating (that is provided as a paint-base coating), but unfortunately, at the same time corrosion resistance decreases.

Consequently, processes to form zinc phosphate coating as a pretreating for painting, are usually carried out in practice laying more importance either on paint bonding quality of the base coating or on corrosion resistance of painted metal. Many attempts have been directed to overcome such inconveniences, but none of them has succeeded in solving the problem up to the present.

In these instances, as a result of elaborate studies and experiments we have found out that, by adding a predetermined quantity of starch, or derivative of starch, or polysaccharides produced by acid decomposition of starch or its derivative to commonly used acid treating solution for zinc phosphate coating, it becomes possible to get a zinc phosphate coating which being free from any defect such as found in coatings by prior art, and being able to satisfy both practical requirements in paint adhesiveness and in corrosion resistance, without any fear of cracking or falling-off of the paint film by bending or cramping, and finally assures extremely long period of endurance to painted articles.

As the present stage it is not yet definitely clear the reason why starch or like additives afford such desirable effects, but is is believed that, by virtue of protective colloid effect, inhibitor effect and viscosity increasing effect as their natural characteristics, metal ions, dissolved out from a metal are brought under action of protective colloid in such a way that, velocity of hydrolysis $Zn(H_2PO_4)_2 \rightarrow Zn_3(PO_4)_2$ due to uprise of pH at the surface of the metal is retarded, crystal growth of zinc phosphate deposited on cathodic part of the metal is properly restricted, and as a result, a coating film of fine and dense structure firmly bound to the metal is obtained. In any case, no matter how the substantial reason may be, it has been determinately proved by our experiments, that these additives, in process of formation of zinc phosphate coating, micronize the crystals of zinc phosphate, properly restricting growth of film so as to enable considerable reduction of coating weight, and accordingly greatly intensify the adhesiveness of the coating film to base metals.

The invention will be better understood from the following description taken in connection with the accompanying drawings in which:

FIG. 1 is a diagram showing adhesiveness of zinc phosphate conversion coatings of the present invention which are applied on zinc galvanized steel sheets, and

FIG. 2 is a diagram showing the weights of said coatings.

FIG. 1 and 2 show respectively adhesiveness and weight of coatings both against change of added quantity of starch or like additives, when zinc phosphate conversion treatments upon zinc galvanized steel panel are processed in acid treating solution for zinc phosphate coating such as described later in our examples added by 0.01–1.0 percent by weight of soluble starch such as starch phosphate, dextrine according to this invention.

As clearly shown in these diagrams, in the neighborhood of 0.05–0.10 weight percent addition of starch or the like material, adhesiveness of coating distinctly increases, while in the neighborhood of 0.10 weight percent addition, weight of coating distinctly decreases, and these facts clearly indicate excellent features of the treating process according to this invention.

Moreover, as shown too in these diagrams, in the zone of more than about 0.1 percent addition of starch or the like, both adhesiveness and weight of coatings change slowly against increase of added quantity, and this fact is very advantageous to operation control over composition of treating solutions in and to quality control over finished products with continuous operation.

Starch or the like materials, which are available as additives according to the feature of this invention, are for example as follows: amylose, amylopectin, dextrin, starch, starch derivatives and, polysaccharides produced from acid decomposition of these, and as said starch derivatives, are included oxidized starch, starch phosphate, nitro-starch, starch sulfate carboxyl starch, hydroxyethyl starch, aminoethyl starch, alkyl starch and aryl starch.

This invention resides in adding one or more of starch or other polysaccharides such as described above by 0.01–1.0 weight percent in total to a usual acid zinc phosphate coating solution.

When the total quantity of additives is less than 0.01 weight percent, there gives no considerable effect upon improvement of coating nor upon reduction of coating weight, while, when said total quantity is increased beyond 1.0 weight percent, this increase is not rewarded by further significant improvement of desired property.

Treating solution according to this invention is obtained only by adding a certain quantity of starch or other polysaccharides to the treating solution. As for treating conditions, including pH value, commonly employed conditions or values are available, and out of them appropriate ones may be selected depending upon the kind of metal to be treated. However, generally speaking, pH in the range of 2 to 3, a temperature in the range of 40° to 70° C., and the treating time, in the case of spraying, from 3 to 10 seconds, while, in the case of dipping, from 5 seconds to 3 minutes, may be adequate.

Hereinafter, descriptions are made about several examples according to this invention.

EXAMPLE 1

Composition of concentrated solution:

H_3PO_4 (75%)	180.5 parts
HNO_3(42° B.)	25.5 parts
ZnO	27.0 parts
$NiCO_3$	37.0 parts
H_2SiF_6(30%)	60.0 parts
HF (70%)	3.2 parts
H_2O	remainder, to make up 1000 parts

Treating solution was prepared by diluting above described concentrated solution in 6 weight percent dilution and by adding 0.01–1.0 weight percent of soluble starch or dextrin. The prepared treating solution was heated to 40°–70° C., and electrogalvanized or hot-dip-galvanized steel panels were subjected to spraying of the heated solution for 3–10 sec. or were dipped in a bath of the heated solution for 5–30 sec. By this treatment, zinc phosphate coating films firmly bound to the surfaces of said panels were obtained.

In contrast, those films which were obtained by using solutions presently in general use or, a diluted solution prepared from said concentrated solution but without additives, over electrogalvanized or hot-dip-galvanized steel panels, were far inferior in paint adhesiveness comparing with that obtained in accordance with present invention.

To compare paint adhesiveness of these two kinds of the treated panels, these panels were subjected to painting by acrylic paint, and after cured, being bent at an angle of 180°, Scotch tapes (trademark of self-adhesive tape) were stuck on the bent parts, then these tapes were rapidly peeled off to test adhesiveness of said paint to treated surfaces in accordance with the method of Japanese Industrial Standard (JIS) G 3312. In case of panels treated according to this invention no change was observed, while, more than 50 percent falling off of the paint was observed in the panels created with prior way. Thus, remarkable difference existing between these two kinds of base coatings are undoubtedly recognized.

EXAMPLE 2

Treating solution was prepared by adding 0.2 g./l. of polyphosphate (such as sodium metaphosphate) and 0.1–1.0 weight percent of soluble starch or dextrin to 6 weight percent aqueous dilution of said concentrated solution shown in example 1. The treating solution was heated to 40°–70° C., and electrogalvanized or hot-dip-galvanized panels were treated with this heated solution by spraying or dipping, and after the treatment, zinc phosphate coatings in the form of fine, dense and uniform crystalline structure, having coating weight of 1.2–1.8 g./m.^{2} and uniform appearance were obtained.

Against this, coating films formed on the surface of electrogalvanized or hot-dip-galvanized panels treated with dilution of the concentrated solution shown in example 1 (without additives), were considerably inferior in fineness, denseness and uniformity of their crystalline structure of the coating, and their coating weight, being 3.5–4.0 g./m.^{2}, were indeed 2–3 times those by this invention, resulting in far less paint adhesiveness.

These panels were subjected to painting in the same manner by acrylic paint and, after cured, subjected to comparative bending test following JIS G 3312. Results of the tests were almost the same as in example 1, and equally indicated the superiority of method of this invention far beyond that of the prior art.

EXAMPLE 3

Composition of treating solution:

Zn	1.6 g./l.
PO_4	5.9 g./l.
NO_3	1.8 g./l.
SiF_6	1.3 g./l.
Ni	1.3 g./l.
H_2O	remainder

The above-indicated treating solution was added with 0.01–1.0 weight percent of starch phosphate, and after heated to 40–70° C., was applied to electrogalvanized or hot-dip-galvanized steel panels by spraying or dipping. Obtained crystalline zinc phosphate coating were fine and uniform structure, having smooth appearance and film weight within a range of 1.2–1.8 g./m.^{2}.

These panels and those treated in prior art fashion in like manner as in the case of example 1 or 2, after painted with acrylic paint and cured, were subjected to comparative bending test. The results were similar as those in examples 1 and 2, panels treated according to this invention are far more excellent in paint adhesiveness than those by prior art. These results of comparison are shown in the following table, in which, also shown results of treating by prior art using polyalcohol or its derivative (e.g. phosphoric ester) as an additive. This last mentioned method by prior art is aimed to arrest decreasing tendency of film weight, in contrast to the feature of this invention which enables considerable decreasing of film weight, and, as shown in the table, this modified method too is far behind this invention in paint adhesiveness.

Comparison between method of this invention

and that of prior art

Coating Process	film weight of zinc phosphate coating	*adhesiveness of painted film
This invention	1.2–1.8 g./m.^{2}	no change observed
Prior art (without additive)	3.5–4.5 g./m.^{2}	more than 50% peeled off
Prior art (with additive of polyalcohol or their derivative)	3.5–4.0 g./m.^{2}	30–50% peeled off

*Tested by method following JIS G 3312, the painted panels were bent at an angle of 180° sandwiching other pieces of plates.

EXAMPLE 4

Composition of treating solution:

Zn	5.5 g./l.
Ni	0.3 g./l.
PO_4	16.4 g./l.
NO_3	4.4 g./l.
H_2O	remainder

Treating solution was heated to 40°–70° C., and after added with 0.01–1.0 weight percent of starch phosphate, was applied to electrogalvanized steel panels by spraying or dipping. The thus obtained zinc phosphate coating was uniform and had fine crystalline structure firmly bound to base metal, having film weight of 0.7–1.5 g./m.^{2}.

In contrast, films obtained by prior method without an addition of starch phosphate were coarse in crystalline structure, lacking uniformity, and coating weight reached at 4.5 g./m.^{2}.

These treated panels were painted by alkydmelamine paint (paint thickness 20μ), and after cured, were subjected to adherence test by Du Pont impact tester. By impacts of, load 1 kg., punch diameter one-half inch and dropping height 20 cm., there observed peelings in panels treated by prior method, while, panels treated by method of this invention did not show any trace of peeling even by impacts of dropping height in 50 cm., thus clearly indicating remarkable superiority to the former.

EXAMPLE 5

Composition of treating solution:

Zn	2.4 g./l.
Ni	0.3 g./l.
PO_4	6.8 g./l.
NO_3	1.6 g./l.
SiF_6	0.4 g./l.
H_2O	remainder

Above solution were heated 40°–50° C., and applied to surfaces of steel panels in two ways, that is, as itself (without addition) and after added with 2–3 g./l. of starch phosphate according to this invention. The weights of coatings obtained in the former case were 2–3 g./m.^{2}, while those of the latter case were decreased greatly down to 0.8–1.2 g./m.^{2}, and moreover, the obtained coatings were far fine, dense and uniform, and firmly bound to the base metal.

These two differently treated panels, after painted with alkyd resin paint of thickness 30μ and cured, were subjected to adhesiveness comparison tests by Du Pont impact tester. Against the fact that, in panels treated in prior way, paintings were failed by impacts of 1 kg. load, ½-inch punch diameter and 20-cm. height and the panels treated according to this invention had overcome impacts from 50-cm. height without any recognizable traces of paint peeling or cracking.

What is claimed is:

1. A method for forming zinc-phosphate-conversion coatings on a metal surface comprising treating said metal surface with an aqueous zinc-phosphate-coating solution having incorporated therein at least one carbohydrate independently selected from the group consisting of starch, starch derivative, and polysaccharides produced by acid decomposition of starch or starch derivatives, wherein said carbohydrate is present in an amount from 0.01 to 1 percent by weight of the solution.

2. The method of claim No. 1 in which said metal is selected from the group consisting of iron, steel, zinc, and zinc alloy.

3. The method of claim No. 1 wherein the treating of a metal surface is performed by spraying the metal surface for 3 to 10 seconds.

4. The method of claim No. 1 wherein the treating is performed by immersing the metal surface for 5 seconds to 3 minutes in the solution.

5. An aqueous composition useful for forming a zinc phosphate conversion coating on a metal surface comprising having incorporated into said composition from 0.01 to 1 percent by weight of the composition a carbohydrate independently selected from the group consisting of starch, starch derivative and polysaccharides produced by acid decomposition of starch or starch derivative.

6. The composition of claim No. 5 wherein the carbohydrate is starch.

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