Feb. 4, 1969 L. STEINBRECHER 3,425,876

PHOSPHATE COATING PROCESS

Filed Oct. 17, 1967



Fig-1

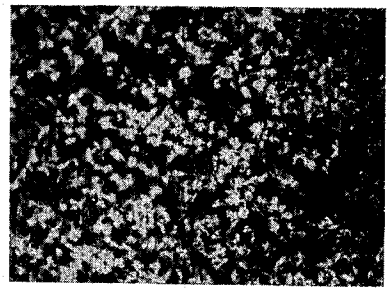


Fig-4

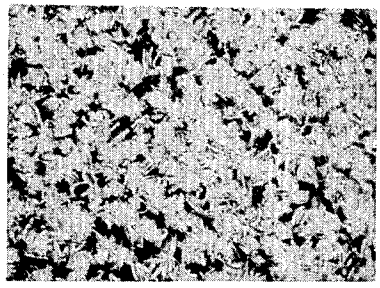


Fig-2

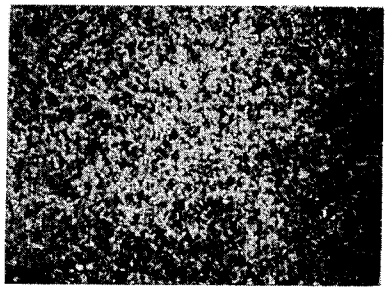


Fig-5

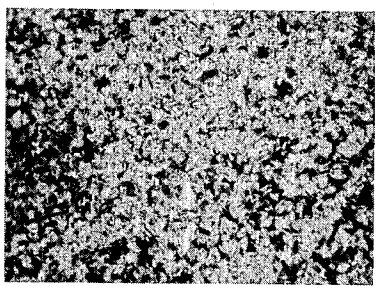


Fig-3

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PHOSPHATE COATING PROCESS

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U.S. Cl. 148—6.15 4 Claims
Int. Cl. C23f 7/14

ABSTRACT OF THE DISCLOSURE

A two-stage process for applying a uniform fine-grained zinc phosphate coating on aluminum surfaces is described. The first stage of the process is treatment of the aluminum surface with an aqueous solution containing, in combined form, titanium and a compound of phosphorus such as, for example, disodium orthophosphate. The second stage of the process is subjecting the pre-treated aluminum surface to a zinc phosphate coating solution containing zinc ion, nitrate ion, phosphate ion, silicofluoride ion, ferrous ion, and fluoride ion. In order to obtain uniform, fine-grained zinc phosphate coatings, it is said that the concentrations of the silicofluoride ion, ferrous ion, and the fluoride ion, must be kept within certain limits. These limits are set forth as: at least 3 grams/liter of silicofluoride ion calculated as SiF_6; from about 0.06 to about 0.2 gram/liter of ferrous ion; and from about 0.01 to about 5 grams/liter of fluoride ion.

This is a continuation-in-part of application Ser. No. 505,432, filed Oct. 26, 1965 now abandoned.

The present invention relates to the art of coating aluminum, and more particularly, it relates to the production of uniform zinc phosphate coatings on surfaces of aluminum and alloys thereof.

Hereinafter in this specification, as well as in the claims appended hereto, use of the term "aluminum" will be understood as applying not only to pure aluminum but also to alloys thereof wherein aluminum is the principal ingredient.

Zinc phosphate coatings on aluminum surfaces are desirable where such surfaces are to be subjected to drawing or other deforming operations. The production of phosphate coatings, particularly zinc phosphate coatings, on aluminum surfaces has been proposed and processes for the production of such coatings are presently in commercial operation. However, certain inherent difficulties have been found to exist in these prior art practices. For example, appreciably heavy and coarsely crystalline zinc phosphate coatings are sometimes obtained and it has been found that these heavy coatings do not lend themselves to subsequent drawing or deforming operations.

These prior art zinc phosphate coatings are obtained through use of solutions which frequently have added thereto complex fluoride compounds, such as for example fluoroborates in the presence of excess boric acid. In some operations, the control of the boron containing constituents has been particularly cumbersome, especially where adequate equipment and trained personnel are not readily available. Thus the commercial utilization of processes of this type falls short of the trouble-free methods sought today in industrial practices.

With the foregoing in mind the principal object of the present invention may be said to reside in the provision of a method for the application of uniform zinc phosphate coatings on aluminum surfaces through the use of a simplified process requiring no complex analytical controls.

Another object of the present invention is the provision

of a method for applying uniform zinc phosphate coating on aluminum surfaces which coatings are especially suitable for drawing or deforming operations.

The above objects together with others may be more readily understood by a consideration of the detailed description which follows together with the accompanying drawings in which FIGURES 1 through 5 are photomicrographs of zinc phosphate coatings. The photographs compare coating of prior art with coatings produced in accordance with the invention and illustrate the superior crystalline structure of the coatings produced by the invention.

The present invention is based upon the discovery that uniform zinc phosphate coatings can be applied on aluminum surfaces through use of a two-stage process consisting of:

(1) Pre-treatment of the aluminum surfaces in an aqueous solution of a complex titanium compound; and

(2) Treatment in a soltion containing ions of zinc, ferrous ion, phosphate, silicofluoride, nitrate and fluoride.

The pre-treatment stage comprises subjecting the aluminum surfaces to the action of an aqueous solution containing from about 0.45 to about 4.5 grams/liter of a compound of phosphorus, and from about 0.005 to about 0.05 gram/liter of titanium. The compound of phosphorus and the titanium are present in a combined form, prepared in accordance with the teachings of one ore more of U.S. Patents 2,310,239, 2,322,349, 2,456,947, 2,462,196, 2,490,062 or 2,874,081. The phosphorus compound may be ortho or pyrophosphate, and the length of treatment may be from several seconds to one minute, or longer at room temperature. One of the preferred compounds is a phosphorus and titanium reaction product produced by the interaction of disodium orthophosphate and a titanium compound such as described in U.S. Patent No. 2,310,239. Another suitable compound includes the reaction product of sodium pyrophosphate and a titanium compound as described in U.S. Patent No. 2,322,349.

Inasmuch as the use of titanium containing pretreatments is well established in the art, suffice it to say that any of the solutions disclosed in the above mentioned patents may be employed in the process of this invention so long as the active constituents are present within the ranges noted above.

Following pre-treatment of aluminum surfaces in an aqueous solution containing the titanium-phosphorus compound, such surfaces are subjected, without any intermediate rinsing, to the action of a conventional nitrate accelerated, zinc phosphate coating solution, containing dissolved silicofluoride ions, and to which has been added dissolved ferrous ions and dissolved free fluoride ions as essential constituents.

The level of dissolved fluoride ion (calculated as F), supplied in the form of hydrofluoric acid or a simple salt thereof, is very important if the desired zinc phosphate coatings are to be obtained, and must be maintained between about 0.01 and about 5 grams/liter. It has been surprisingly discovered that as the fluoride ion concentration increases there is a corresponding decrease in the coating weights obtained on the treated aluminum surfaces. Conversely, where the fluoride ion concentration decreases, appreciably heavier and more coarsely crystalline coatings are realized. For this reason, and to secure uniform coating weights, it is essential that the fluoride ion concentration be controlled at all times so as to provided the desired uniformity of coatings produced.

Between the limits of 0.01 to 5 grams/liter of dissolved fluoride ion, it is possible to obtain coatings which are suitable for a variety of uses, including drawing operations. Where the fluoride ion concentration increases above about 5 grams/liter a greater etching action occurs on

the aluminum surfaces at the expense of coating formation. Where the fluoride ion concentration decreases below about 0.01 gram/liter, very heavy coatings are obtained which are too coarsely crystalline for drawing purposes. Accordingly, control of the fluoride ion concentration (calculated as F), all other parameters otherwise controlled, permits attainment of uniform coatings of varying weights.

One method for controlling the simple fluoride concentration is through use of a lime soda-glass etch rate test, such as described in U.S. Patent 2,814,577, assigned to the same assignee as this invention. However, the preferred method of control involves use of a silicon electrode device such as is described in one of the following of my U.S. patents, 3,129,148, 3,329,587, and 3,350,284, all of which are assigned to the same assignee as this invention.

So far as concerns the ferrous ion concentration, it has been found that if this component is used without the benefit of the titanium-phosphorus compound pre-treatment, the fine, uniform coatings will not be obtained. Conversely, if the titanium pre-treatment is used, but no ferrous ion is added to the zinc phosphate coating bath, the improvements of this invention will not result. It is essential that both of these conditions be met in accordance with the teachings indicated hereinabove.

The amount of ferrous ion (calculated as Fe) which is employed is critical so far as coating weights are concerned and must be within the range of from about 0.06 to about 0.2 gram/liter. If the ferrous ion content falls below about 0.06 gram/liter the coatings which are obtained will be very coarse and crystalline, and will not be suitable for subsequent use in deforming or drawing operations. Conversely, where the amount of ferrous ion exceeds the upper limit of about 0.2 gram/liter, the subsequently obtained coatings will be very sparse and of little or no value in providing protective coatings on aluminum surfaces, particularly when such surfaces are subjected to subsequent drawing operations.

In order to demonstrate the improved coatings obtained by the process of this invention, there is presented below a comparison of results obtained in accordance with the teachings of this invention with results derived from the exclusion of one of the critical operating stages or bath constituents. These results, however, are presented solely by way of illustration and are not intended to be construed as in any way limiting the scope of this invention except as defined in the appended claims.

Separate aqueous phosphate coating solutions were prepared in accordance with the following table and were utilized for the coating of clean aluminum panels, utilizing temperatures of 60° C. and 6-minute cycles. Where pre-treatments were employed, in accordance with the teachings of this invention, such pre-treatments consisted of utilizing aqueous solutions of a complex titanium compound prepared so as to contain 0.045% of disodium orthophosphate and 0.0005% titanium radical in accordance with the teachings of U.S. Patent No. 2,310,239. The pre-treatment was conducted utilizing a 20-minute immersion cycle at room temperature.

TABLE I

Process	1	2	3	4	5
Titanium pre-treatment	No	Yes	Yes	Yes	Yes
Phosphate coating bath:					
G./l PO_4	25	25	25	25	25
G./l NO_3	17	17	17	17	17
G./l Zn	15	15	15	15	15
G./l SiF_6	4.5	4.5	4.5	4.5	4.5
G./l Fe	0.1			0.1	0.1
G./l F	0.5		0.5		0.5
Coating weight mg./ft.^{2}	2,475	2,560	1,650	1,185	871

Coating appearance:
1. Very coarsely crystalline uneven.
2. Coarsely crystalline.
3. Coarsely crystalline.
4. Coarsely crystalline.
5. Very fine, uniform.

The addition of SiF_6 ions was effected utilizing the sodium salt (Na_2SiF_6). Other alkali metal or the ammonium salt may be employed, or fluosilicic acid (H_2SiF_6) may be used if desired. The minimum amount of silicofluoride ion, calculated as SiF_6, which must be present has been found to be about 3.0 g/1. Where smaller quantities are used the coatings produced on aluminum will be very uneven, leaving large areas of uncoated metal surfaces. So far as concerns an upper limit of SiF_6, this has been found to be limited solely by solubility considerations. However, in the interests of obtaining excellent results consistent with this invention, while simultaneously preventing waste, it has been found preferable to employ from about 4 to about 6 g./l. of SiF_6. It has been found that the use of silicofluoride is essential, and that other complex fluorides which have heretofore been regarded as similar to it in operation in coating baths are not satisfactory. For example, it has been found that while silicofluoride is very satisfactory in operation, both fluotitanate and fluozirconate are inoperative.

After coating and drying each treated panel was inspected under a microscope, and was photomicrographed at 200×. FIGURE 1 is the photomicrograph at the above magnification of the panel treated by the bath of Process 1. FIGURES 2, 3, 4, and 5, are photomicrographs at the same magnification of panels treated by processes 2, 3, 4, and 5, respectively.

Although the microscopic examination did not reveal the three-dimensional nature of the surface coatings, it was apparent that the coatings on Panel 1 were grossly crystalline and very uneven in appearance, as shown in FIGURE 1. On the other hand, the coating produced from the solution containing both ferrous ion and simple fluoride ion was not only uniformly apportioned across the surface of the aluminum panel, but was of a highly desirable fine grained, crystalline structure suitable for use in drawing operations, as shown in FIGURE 5. Microscopic examination of Panels 2, 3, and 4 revealed coarsely crystalline coatings showing the effects of omitting one or more of the essential ferrous ion and fluoride ion components from the phosphate coating stage, as appears in FIGURES 2, 3, and 4. The effect of omitting the titanium pre-treatment stage appeared clearly from the radically differing crystal structures of Panels 1 and 5, shown in FIGURES 1 and 5. Finally, the microscopic study showed that utilization of a titanium pre-treatment but exclusion of the ferrous and fluoride ions from the phosphate coating stage also failed to produce the highly uniform and finely grained crystalline coatings, as can be seen by comparison of FIGURES 2 and 5.

In order to illustrate the effects of varying amounts of ferrous ion in the phosphating stage of the process of this invention there are presented below, in Table II, the results obtained by varying the ferrous ion concentration over a wide range. A process similar to that described under column 3 of Table 1 was employed and to various portions of the phosphate coating bath there was added ferrous sulfate ($FeSO_4 \cdot H_2O$) so as to obtain the indicated amount of dissolved Fe. These results are shown below.

TABLE II

Gram/liter Fe	Coating wt., mg./ft.^{2}	Observation on coating
None	1,975	Coarsely crystalline.
0.02	1,974	Do.
0.04	1,520	Do.
0.06	1,124	Uniform fine crystals.
0.08	1,059	Uniform fine grain.
0.10	901	Do.
0.12	703	Do.
0.16	652	Do.
0.20	608	Do.
0.80	395	Do.
2.0	250	Do.

The effects of increasing dissolved ferrous ion concentration on coating weight, as seen from the foregoing table, has been totally unexpected in view of the well

known fact that ferrous ion, dissolved in coating phosphate solutions for steel, has been known to produce heavy grained, coarsely crystalline coatings.

In connection with Table II, it should be noted that the coating weight falls off materially when the ferrous ion concentration is raised above 0.2 grams/liter. Thus, while uniform, fine grained structure is still obtained at high ferrous ion concentrations, the coating is very sparse and of little value in providing protection to the aluminum, especially when it is subjected to later drawing operations.

From the foregoing results it is readily apparent that the process of the present invention is capable of providing a highly desirable, uniform, fine grained zinc phosphate coating for aluminum, which coating is suitable for use in drawing operations.

I claim:

1. The method for forming a uniform fine-grained zinc phosphate coating on aluminum surfaces comprising first contacting the surface with an aqueous pre-treatment solution containing from about 0.45 to about 4.5 grams/liter of a compound of phosphorous and from about 0.005 to about 0.05 gram/liter of titanium, said compound of phosphorous and titanium being present in combined form and then contacting said surface with an aqueous coating solution, the essential ingredients of which are

zinc ion, nitrate ion, phosphate ion, at least about 3.0 g./l. of silicofluoride ion, calculated as SiF_6, from about 0.06 to about 0.2 gram/liter ferrous ion, and from about 0.01 to about 5 grams/liter of fluoride ion.

2. The method in accordance with claim **1** wherein said surface is contacted with said aqueous coating solution while still wetted with said aqueous pre-treatment solution.

3. The method in accordance with claim **1** wherein silifluoride ion is present in amounts from about 4 to about 6 g./l. calculated as SiF_6.

4. The method in accordance with claim **1** wherein the compound of phosphorous is disodium orthophosphate.

References Cited

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2,312,855	3/1943	Thompson	148—6.27 X
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RALPH S. KENDALL, *Primary Examiner.*

U.S. Cl. X.R.

148—6.27