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(54) **Method of forming phosphate coatings on zinc**

(57) White specking on galvanised or other zinc surfaces during zinc phosphate coating is reduced or eliminated by including fluoride, preferably as complex fluoride, in a ratio fluoride ions:chloride ions of at least 8:1.

**GB 2 179 680 A**

## SPECIFICATION

**Method of forming phosphate coatings on zinc**

- 5 It has been known for about seventy years to form phosphate coatings on a zinc surface by contacting the surface with an aqueous acidic phosphate solution. Typical solutions currently used for this purpose include phosphate, zinc and/or manganese, and typically one or more of nickel, cobalt, copper, nitrate, nitrite, fluoroborate and silico fluoride. Before treatment with this solution the surface may have been cleaned and may have been subjected to a conditioning step, and the surface may also be subjected to one or more post treatments. The resultant coating provides useful properties when the surface is to be subjected to deformation and provides a protective base when the surface is to be painted. However certain problems can arise. 5
- 10 One problem is that when some paints are applied over the coatings the paint coating develops a roughness which is referred to as hazing and the gloss may not be as high as is desirable. Also the painted surface, when subjected to bending, may have unsatisfactory resistance to flaking and cracking. 10
- 15 Another problem associated with such coatings, particularly when they are deposited on galvanised surfaces, is known as "white specking" or "nubbing". This phenomenon can best be described as uncontrolled crystal growth at pinpoint locations. This growth results in a flawed, rough surface. The specks appear as large white growths; they are generally zinc or zinc/iron phosphate crystals. While they can vary greatly in size, they are typically 50–150  $\mu\text{m}$  wide and 100–400  $\mu\text{m}$  high. 15
- 20 The larger crystal growths are apparent to the naked eye from virtually any angle. The smaller growths can only be seen with some magnification. However, when the treated or coated metal surface is painted, such flaws are immediately apparent and the resulting product is frequently unacceptable. A uniform paint film cannot be applied; this is true whether the paint is applied by spray or electrodeposition. The "white specking" has been observed to occur during both the pre-treatment and treatment stages. However, it most commonly appears during the treatment stage. 20
- 25 There have been many attempts to effectively solve this problem of coating zinc surfaces, particularly galvanised surfaces; all such attempts have focused on the treatment steps. Two of the most effective are described in U.S. 3,240,633 and U.S. 2,835,617 and involve the introduction of fluoride and ferric ion into the treatment solution. 25
- 30 For economic and environmental reasons it is desirable to keep the amount of fluoride as low as possible. However experience has shown that the presence of fluoride can assist in the prevention of white specks or nubbing although abnormal crystal growth often still does occur, especially at the environmentally desirable low levels of fluoride. 30
- 35 We have now determined that the problem of white specking or nubbing is due, at least to a significant extent, to the presence of chloride ion but that its effect can be counteracted by fluoride, the amount of fluoride that has to be present to reduce or eliminate white specking or nubbing depending upon the concentration of chloride. Thus an increase in chloride without a corresponding increase in fluoride will result in more white specking or nubbing. It has not previously been appreciated that the addition of fluoride in an amount proportional to the amount of chloride that is present, and in particular the absolute minimisation of the amount of chloride that is present, could lead to elimination of the problem of white specking. 35
- 40 Many phosphating baths contain relatively high concentrations of chloride. For instance the make-up water may contain chloride and chloride compounds may be deliberately added. For instance sodium chloride may be incorporated as a bulking or anti-caking agent in the additives that are used to make the working solution and desired cations may be introduced as the chloride, e.g., ferric chloride in U.S. 3,240,633. Further, chlorate is a common accelerator and during use this tends to decompose to generate chloride. The fact that this can be undesirable has been mentioned in the literature, namely in GB 2,136,455A in the context of a process of forming an iron phosphate coating on a ferrous substrate and in GB 2,137,231A in the formation of a light zinc phosphate coating by treatment with an appropriate acidic zinc phosphate solution that contains nitrite and water soluble organic nitro compound, optionally with nitrate, as accelerator and that may contain other additives, for example selected from Ni, Co, Cu, Mn, Ca, Mg, Fe, Na, K, Li,  $\text{NH}_4$ ,  $\text{SO}_4$ , F,  $\text{BF}_4$ ,  $\text{SiF}_6$ , citrate and tartrate. The process is described for various surfaces including zinc or steel. The only example is concerned solely with the treatment of steel and the only additive that is incorporated, out of the list given above, is Ni. No specific amounts of chloride are mentioned in either of these patents and so neither of them is of any assistance in considering how to solve the problem of white specking in the zinc phosphating of galvanised or other zinc surfaces. 40
- 45 In the invention a phosphate coating is formed on a zinc surface by contacting the surface with an aqueous acidic metal phosphate solution, where the metal is selected from manganese and zinc, containing fluoride in an amount of 0.01 to 3% by weight and in which the weight ratio fluoride:chloride is at least 8:1 and is such as to substantially reduce white specking in the coating. 45
- 50 Preferably the amount of phosphate ion is 0.5 to 4%, the amount of zinc and/or manganese ions is such that dihydrogen phosphate is formed with substantially all of the phosphate ions, and the solution contains 0.01 to 1% fluoride ions and the fluoride ions are present as complex fluoride ions. 50
- 55 The ratio of fluoride:chloride must be at least 8:1 and may need to be higher if satisfactory elimination of white specking is to be achieved, particularly when the chloride ion content is undesirably high. If at any particular ratio white specking is still found to be a problem then the ratio should be increased. Generally the ratio is greater 55
- 60 60
- 65 65

than 10:1 and preferably it is greater than 14:1. Preferably it is below 50:1, often below 30 or 35:1. By appropriate choice of the ratio it is possible substantially to eliminate abnormal crystal growth whilst at the same time keeping the amount of fluoride satisfactorily low. Thus in the invention it is possible to maximise the effect of the fluoride while minimising the amount that has to be used.

- 5 It is preferred that the treatment solution contains less than 50 ppm chloride (i.e., less than 0.005% chloride) and where possible even lower values are desirable since this minimises the amount of fluoride that is required. In particular it is preferred that the amount of chloride is below 30 ppm or 0.003% and most preferably below 20 ppm or 0.002%. Best results are obtained when the amount of chloride is below 15 ppm or 0.0015%. 5
- In order to permit efficient operation of the process, with minimum usage of fluoride, the ratio of  
10 fluoride:chloride should be maintained at the desired level during the process. In order to minimise the amount of fluoride that has to be added it is desirable to measure the amount of chloride and then select the amount of fluoride in response to the measured amount of chloride. Measurement may occur merely at start up, provided the conditions and materials are constant, but will generally be conducted from time to time during the process. 10
- The amount of phosphate ions in the solution is preferably 0.5 to 2.5%, most preferably 0.5 to 2%. The solution  
15 may contain manganese and/or zinc, but generally contains zinc. The amount should be at least sufficient to form dihydrogen phosphate. 15
- The solution optionally contains nitrate ions, at a level of 0.025 to 2%, and more preferably 0.05 to 1%. It will be appreciated that some level of nitrate ion may be generated in the coating step of the present invention even if it is not added. However, controlled addition is preferred.
- 20 The phosphate and nitrate may be added to or introduced into the solution from any conventional source. The solution optionally contains nickel ions and/or cobalt ions, preferably at a level of 0.01% to 1%. 20
- The nickel or cobalt ions may be introduced as salts such as the sulphate, phosphate, carbonate or nitrate salts, preferably as the carbonate salt.
- The solution contains about 0.01 to about 3% complex fluoride ion. More preferably, the complex fluoride ion  
25 is present at a level of about .025 to about 0.25%. It will be appreciated that the higher the ratio of zinc surface to steel surface to be treated, the higher the desirable fluoride level. Thus, for example, when treating galvanised surfaces (greater than 50%), level of about 0.05 to about .2%, and more preferably about 0.075 to about 0.2, and still more preferably about 0.08 to about 0.15%, are employed. These levels are preferably measured by employing a fluoride sensitive electrode such as one manufactured by Orion. 25
- 30 The complex fluoride ion may be added to or introduced into the solution from any conventional source, including those discussed in U.S. 2,835,617 and U.S. 3,240,633. While free fluoride ion may be employed under certain circumstances, it is preferred that the fluoride ion be a complex (or complexed) fluoride ion, most preferably silico fluoride. The silico fluoride ion provides especially superior results when used on continuous hot dip zinc surfaces, and since they are readily available commercially and provide both the necessary fluoride concentration and concurrently  
35 supply other beneficial ions, it may be, in many instances, much more desirable to formulate the compositions with silico fluoride as the starting materials rather than, for example, free fluoride ion sources such as hydrofluoric acid. 35
- Although, for instance, nickel, cobalt and/or iron cations could be introduced as chloride in small amounts this is undesirable as it inevitably results in an increased chloride concentration in the solution.
- It is known that the incorporation of ferric ion in aqueous acidic metal phosphate solutions is effective to  
40 substantially reduce the coating weight which is obtained over a wide range of solution acidities. It has also been noted by the art that solutions having total acid values in the range of about 10 to about 110 points are effective to form adherent protective coatings and are improved by the addition of the ferric ion. Points of total acid refers to the number of ml of N/10 NaOH required to titrate a 10 ml sample of the solution to a phenolphthalein end point. 40
- 45 The solution may be applied to the surface to be coated by spraying, roller coating, by atomizing the solution on a preliminarily heated zinc surface or by dipping the part to be coated in a tank containing the use solution. Solutions will form coatings in the range of about 44°C to the boiling point of the solution but are preferably operated in the range of about 55°C to 82°C with the best overall results being obtained with solutions at about 65°C for spray, roller coating, or atomizing, and 44 to 55°C for dip application. 45
- 50 The metal surface is subjected to various treatments before the phosphating process and unacceptably high chloride concentrations in these pretreatments can cause white specking, for instance as a result of chloride being carried into the treatment solution and raising the chloride level of that solution to an unacceptable level. Accordingly when the surface is contacted with one or more aqueous pretreatment liquids before the metal phosphating treatment it is preferred that the pretreatment liquid or substantially all the pretreatment liquids should be  
55 substantially free of chloride, preferably having a chloride concentration of below 100 ppm and most preferably below 50 ppm. By saying that substantially all the pretreatment liquids should be substantially free of chloride we mean that the latter, and especially the last, pretreatment liquids should be substantially free of chloride. The chloride content of an early pretreatment liquid, for instance that is subsequently followed by several chloride-free pretreatments, is less important. The pretreatment liquids may be selected from cleaners (such as alkaline cleaners  
60 and aqueous rinses), conditioners or activators and cleaner/conditioner combinations as well as aqueous rinses. 60
- In particular it is common to subject the metal surface to a titanium or high phosphate rinse solution as a conditioning or activating treatment, and this solution should be substantially free of chloride, preferably below 50 ppm chloride. Unless special precautions are taken conventional conditioning rinses, e.g., as made by neutralisation of titanium sulphate with caustic soda followed by phosphoric acid, will contain high chloride  
65 levels, often above 400 ppm chloride. 65

In general it is desirable that all concentrates, additives, replenishments, rinses or combination agents used in the pretreatments and phosphate coating processes should be substantially free of chloride, below 100 ppm and preferably below 500 ppm and most preferably below 30 ppm chloride.

When cleaners are to be used to remove grease, dirt or particulate material in conventional manner they may be mild or strong alkali cleaners or acidic cleaners and may be followed and/or preceded by a water rinse. After cleaning condensed phosphate pretreatment solutions containing a small quantity of titanium or zirconium may be applied, suitable processes being described in U.S. 2,310,239, 2,874,081 and 2,884,351.

After forming the metal phosphate coating, it is advantageous, particularly in those cases in which the coated surface is to be subsequently painted, to rinse the coating in a dilute aqueous chromic acid solution of conventional constituency, for example, one containing about 0.025 to 0.1% chromium ion as Cr<sup>+3</sup>, Cr<sup>+6</sup> or mixtures thereof. Another class of useful rinses which may be applied to the part or workpiece after the application of the coating are disclosed in U.S. patent nos. 3,975,214; 4,376,000; 4,457,790; 4,039,353; and 4,433,015. In summary, the post-treatment compound placed into the rinse is a poly-4-vinyl-phenol or the reaction produce of poly-4-vinyl-phenol with an aldehyde or ketone.

After such a final chromic acid or poly-4-vinyl-phenol rinse, the coatings have good resistance to corrosion prior to the application of paint and when painted have been found to be more resistant to cracking, chipping and peeling when the painted surface is deformed such as by forming to final desired shape in dies, by bending or the like.

The following is an example.

Galvanized panels were processed using an immersion zinc phosphate bath in the cycle outline. Chloride and fluoride were gradually introduced into the zinc phosphate bath as solutions of "tap" water and sodium chloride or sodium silica fluoride, respectively. The chloride level was increased until "white specking" was observed at which point fluoride was then added until the white specking vanished. This cycle was then repeated using the previously altered zinc phosphate bath. To verify results, a fresh zinc phosphate bath was contaminated with an initial charge of chloride greater than necessary to produce "white specking" and fluoride added until the "specking" had vanished. Panels were then examined for coating weight, crystal size and coating appearance.

#### *Laboratory Process Cycle*

##### *Stage 1 – Alkaline Cleaner:*

30	Conventional Cleaner		30
	Concentration	– 1/2 ounce per gallon (4 g/l)	
	Temperature	– 60°C	
35	Time	– 120 seconds spray	35

##### *Stage 2 – Warm Water Rinse:*

40	Temperature	– Ambient	
	Time	– 100 seconds spray	40

##### *Stage 3 – Titanium-containing Surface Conditioner:*

45	Concentration	– 1.5 g/l; pH = 9.2; 15 ppm Ti	
	Temperature	– Ambient	45
	Time	– 100 seconds Immersion	
	Chloride concentration	– less than 50 ppm	

##### *Stage 4 – Zinc Phosphate Bath:*

50	Concentration or Test	– Free Acid – 1.0 points – Total Acid – 20.0–22.0 points – Accelerator – 3.0–3.5 points	50
	Temperature	– 55°C	
55	Time	– 240 seconds Immersion	55

##### *Stage 5 – Cold Water Rinse:*

60	Temperature	– Ambient	
	Time	– 100 seconds Immersion	60

##### *Stage 6 – Oven Dry:*

65	Temperature	– 120°C	
	Time	– 5 minutes	65

*Results*

TABLE 1

		Stage 4 Bath Analysis				
	Sample	Specking	Chloride	Fluoride	F <sup>-</sup> :Cl <sup>-</sup> Ratio	
5	Fresh	No	32 ppm	1000 ppm	31.3:1	5
10	After 0.34 Grams NaCl	Slight	80 ppm	1100 ppm	13.8:1	10
15	After 0.6 Grams Na <sub>2</sub> SiF <sub>6</sub>	No	86 ppm	1400 ppm	16.3:1	15
	After 0.2 Grams NaCl	Slight	108 ppm	1200 ppm	11.1:1	
20	After 0.6 Grams Na <sub>2</sub> SiF <sub>6</sub>	No	104 ppm	1400 ppm	13.5:1	20
	Fresh	No	< 10 ppm	900 ppm	—	
25	After 0.8 Grams NaCl	Heavy	104 ppm	900 ppm	8.6:1	25
	After 0.6 Grams Na <sub>2</sub> SiF <sub>6</sub>	Slight	104 ppm	1000 ppm	9.6:1	
30	After 3.34 Grams Na <sub>2</sub> SiF <sub>6</sub>	No	98 ppm	1400 ppm	14.3:1	30

*Claims*

- 35 1. A process in which a phosphate coating is formed on a zinc surface by contacting the surface with an aqueous acidic metal phosphate solution, where the metal is selected from manganese and zinc, containing 0.01 to 3% by weight fluoride and in which the weight ratio fluoride/chloride is at least 8:1 and is such as to substantially reduce white specking in the coating. 35
2. A process according to claim 1 in which the ratio is at least 10:1.
- 40 3. A process according to claim 1 in which the ratio is at least 14:1. 40
4. A process according to any preceding claim in which the solution contains chloride in an amount of below 0.005% by weight.
5. A process according to any preceding claim in which the solution contains chloride in an amount of below 0.002% by weight.
- 45 6. A process according to any preceding claim in which, before the application of the metal phosphate solution, the surface is subjected to pretreatment by a conditioning solution and this solution contains chloride in an amount of below 100 ppm. 45
7. A process according to any preceding claim in which the surface is contacted with one or more aqueous pretreatment liquids before contact with the metal phosphate solution and in which the pretreatment liquid or 50 substantially all the pretreatment liquids have a chloride content of below 100 ppm. 50
8. A process according to claim 6 or claim 7 in which the or each pretreatment liquid has a chloride content of below 50 ppm.
9. A process according to any preceding claim in which the content of chloride in the metal phosphate solution is measured and the amount of fluoride is selected in response to the measured amount of chloride.
- 55 10. A process according to any preceding claim in which the amount of phosphate is from 0.5 to 4%, the amount of zinc and/or manganese is at least sufficient to form dihydrogen phosphate with the phosphate ions and the amount of fluoride is from 0.01 to 3%. 55
11. A process according to any preceding claim in which the amount of phosphate is from 0.5 to 2%.
12. A process according to any preceding claim in which the metal phosphate solution contains nitrate in an 60 amount of from 0.025 to 2% by weight. 60
13. A process according to any preceding claim in which the metal phosphate solution contains from 0.01 to 1% by weight of metal ions selected from cobalt and nickel ions.