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SURFACE TREATMENT OF METALS

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This invention is concerned with phosphating compositions for use in the surface treatment of metals as by spraying, brushing, or immersion. More particularly, and indeed exclusively, this invention is concerned with improvements in phosphating compositions comprising essentially an aqueous solution containing orthophosphate ions, the cations of zinc as the coating metal, and an oxidising accelerator, such later solutions, which are well known in the art, being hereinafter referred to as accelerated zinc orthophosphate coating solutions.

There is at the present time an increasing demand, particularly amongst manufacturers of automobile bodies and other pressed steel articles, for phosphate coatings which, while exhibiting comparable corrosion resistant properties, are of lighter weight than the coatings obtainable by the use of present commercially available accelerated zinc orthphosphate coating compositions.

In accordance with the present invention, it has now been discovered that the coating weight produced by the use of accelerated zinc orthophosphate coating solutions may be markedly reduced without prejudicial sacrifice of anti-corrosion properties by providing, as an addition to such solution, a relatively small quantity of a molecularly dehydrated orthophosphoric acid or soluble salt thereof.

The effect of the additions of this invention is to decrease the crystal size of the formed coating and to permit of the production of a complete phosphate coating having an appreciably reduced weight per unit area, it being understood that by "complete" phosphate coating is meant a coating having a weight which is the maximum possible attainable under the conditions of treating being employed.

The improvements referred to herein are obtainable by the use of any molecularly dehydrated orthophosphoric acid or a suitable soluble salt thereof, "suitable" salts being those which while possessing the requisite dehydrated othophosphate portion, will not introduce into the solution any other material which will vitiate the coating action of the solution, e.g. substantial amounts of copper or other metal which plate out on the surface under treatment and thus impair corrosion-resistance. Thus in practising the invention, there may be employed metaphosphoric acid, metaphosphates and polymetaphosphates, pyrophosphoric acid, pyrophosphates and polypyrophosphates. Examples of specific salts which may be added to an accelerated zinc orthophosphate solution in accordance with this invention are the following: sodium hexametaphosphate, zinc metaphosphate, ammonium metaphosphate, zinc pyrophosphate and calcium pyrophosphate.

Hydrogen ions in amounts greater than those required to produce a coating action and hold the essential coating constituents in solution are relatively undesirable in phosphating solutions, a fact which has been established to be due to the extremely high diffusion coefficient of the hydrogen ion. Hence it is preferred that the additions of this invention should be made in the form of salts rather than free acids. Other higher diffusion coefficient cations—specifically those having a diffusion

coefficient as great or greater than that of the lithium ion—are likewise relatively undesirable, amongst such undesirable cations being those of ammonium, sodium and potassium. It further follows therefore that, on technical grounds, salts which ionise in solution to yield those last mentioned high diffusion coefficient cations are less preferred than those yielding low diffusion coefficient cations such as those of zinc and nickel. However, economic consideration may override purely technical considerations and it may be expedient to employ a sodium salt such as sodium hexametaphosphate on the ground that it is cheaper and more readily available than a suitable zinc salt such as zinc metaphosphate.

Regarding the quantity in which the additions are employed this is in general appreciably less than the quantity of orthophosphate (calculated as PO_4) present in the solution. Good results may be achieved in practice by using for each litre of the coating solution from about 0.01 to 1.0 gm. or even more, particularly from 0.05 to 1.0 gm., of dehydrated orthophosphate calculated as PO_3 or P_2O_7 as the case may be. As a general rule, no advantage is to be gained from using more than 1.0 gm./litre of PO_3 or P_2O_7 since no further diminution in crystal size is usually obtained and the treatment time to produce complete coverage tends to be increased.

Additions of pyrophosphoric acid or soluble salts thereof produce a marked diminution of crystal size, the coating otherwise retaining the conventional appearance. Additions of metaphosphoric acids or soluble salts thereof up to approximately 0.4 gm. per litre (as PO_3) have similar effects to the additions of pyrophosphoric acid or its salts. Additions of metaphosphoric acid or soluble salts of that acid greater than 0.4 gm. per litre (as PO_3) produce a change in general appearance of the coating, in that there is a gradual appearance of white microspheres which increase in number with increasing concentration of PO_3 until, at a concentration of approximately 1.0 gm. per litre PO_3, the entire coating appears to consist of those white microspheres. It is probable that these white microspheres are agglomerates of vary small crystals indeed and their appearance does not necessarily indicate a change in crystal structure. In any case a coating, consisting of these apparent agglomerates has desirable properties, both from paint-bonding and high corrosion resistant value standpoints. Salt of metaphosphoric acid are therefore the preferred additions to be made under this invention.

Steps should of course betaken to maintain the concentration of dehydrated orthophosphate material within operative limits throughout the period of use of the phosphating solution and this can be achieved by incorporating additional dehydrated orthophosphate material as and when the usual replenishment operations are conducted. With regard to the maintenance of an operative concentration of dehydrated orthophosphate ions, a fact to which consideration should be given is that dehydrated orthophosphates are not completely stable and are converted over a period of time to orthophosphates.

Typical accelerated zinc orthophosphate solutions to which the additions of the present invention are applicable are those having a formulation within the general and preferred ranges given below:

	General Range	Preferred Range
Free Acid	1-8 Points [1]	2-3 Points.[1]
Total Acid	15-80 Points [2]	18-25 Points.[2]
Nitrate (as NO^3)	3-30 gms./litre	7-14 gms./litre.
Zinc	3-24 gms./litre	5-6 gms./litre.

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[1] Free acid "points"=number of mls. of N/10 NaOH for a methyl-orange end point when titrating 10 mls. of solution.

[2] Total acid "points"=number of mls. of N/10 NaOH required to reach a phenolphthalein end point when titrating 10 mls. of solution.

The benefits yielded by the additions of the present invention will be at once evident from the results of the experiments reported below.

Experiment I

A zinc orthophosphate solution was made up having a total acid pointage of 20 and a free acid pointage of 2.5 (at 90° C.). The zinc and nitrate (NO_3) content of this solution were 6.0 and 7.0 gms./litre respectively. When a series of CRCA (cold rolled, cold annealed) steel test panels were immersed in this solution for ten minutes each to give a "complete" phosphate coating, the average coating weight was 1460 mg./sq. ft. When the experiment was repeated, this time with the addition to the solution of 0.5 gm./litre of sodium hexametaphosphate, a complete phosphate coating was again obtained in the ten minute treating period but the coating weight was reduced to an average of 100 mg./sq. ft.

Experiment II

A zinc orthophosphate solution was made up and such solution contained, for each litre thereof, 6.0 gms. Zn, 7.0 gms. PO_4, 7.0 gms. NO_3 and 0.5 gm. F (added as ZnF_2). Treatment of test CRCA steel panels by immersion in a bath of this solution at a temperature of 70° C. for a period of 3 minutes produced a "complete" phosphate coating having a weight of about 500 mgs./sq. ft. This experiment was then repeated except that to the solution was added 0.56 gm. per litre of zinc metaphosphate (=0.4 gm./litre PO_3) and in this case there was obtained after the three minute treatment period a visibly "complete" phosphate coating having a weight of only about 100 mg./sq. ft.

In the second of the experiments given above the zinc orthophosphate coating solution employed contained simple fluoride ions, since the invention is particularly applicable to accelerated zinc orthophosphate coating solutions containing from 0.1 to 1.0, preferably 0.2 to 0.6 gm./litre of simple fluoride ions.

Regarding the oxidising accelerators employed in the practice of the invention, any of those known in the art may be used, but those preferred are nitrogenous oxidising accelerators particularly nitrates or their equivalents such as nitroguanidine. Other accelerators which may be used are chlorates, either alone or in admixture with nitrates.

The improved solutions of this invention may be applied in any of the usual ways, preferably by immersion of the surface to be treated, and may be applied to any metallic surface commonly treated with accelerated zinc orthophosphate solutions, namely surfaces composed of iron, zinc, cadmium and alloys of these metals. Usually the solutions will be employed at elevated temperatures such as 70–95° C.

In conclusion it may be stated that the additions of this invention, apart from reducing coating weight without impairing anti-corrosion value, seem to cause a marked reduction in the quantity of sludge formed during the treating process. This reduction in sludge formation coupled with the relatively low weight of the coatings formed is responsible for a material saving in the consumption of phosphating chemicals. The light-weight "complete" coatings yielded by the improved phosphating compositions of the invention, have particularly desirable properties in that they will withstand a very considerable degree of distortion, during the course of forming operations on the article to which they are applied, without undergoing destruction of their anti-corrosion properties.

Apart from the new and improved solutions per se, this invention also includes processes for treating metallic surfaces with the new solutions in any of the ways indicated above. The invention further includes concentrates which on dilution with water yield the improved solutions in a ready-for-use condition. Such concentrates consist of an aqueous solution containing all the active ingredients of the eventual solution and they have a total acid pointage of at least 150 so as to require dilution several times e.g. 10–25 times, to form a ready-for-use solution.

We claim:

1. A process which comprises forming a crystalline essentially zinc orthophosphate coating upon the surface of a metal selected from the group consisting of iron, zinc, cadmium, and alloys of such metals, by treating the surface with an aqueous solution of zinc dihydrogen orthophosphate containing nitrate ions and conforming to the following formulation:

Free acid	points	1–8
Total acid	do	15–80
Nitrate (as NO_3)	grams/litre	3–30
Zinc	do	3–24

wherein said aqueous solution also has dissolved therein a phosphate material selected from the group consisting of molecularly dehydrated orthophosphoric acids and soluble salts of such acids, said phosphate material being present in the solution in an amount, calculated as PO_3, in the range from 0.01 to 1.0 gram/litre of solution, and the composition of said solution being maintained throughout its period of use to produce said crystalline coating consisting essentially of zinc orthophosphate.

2. A process as claimed in claim 1, wherein said phosphate material is selected from the group consisting of metaphosphoric acid, and meta- and polymeta-phosphates.

3. A process as claimed in claim 1, wherein said phosphate material is sodium hexametaphosphate.

4. A process as claimed in claim 1, wherein said solution also contains from 0.1 to 1.0 gram/litre of simple fluoride ions.

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