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PRODUCTION OF PHOSPHATE COATINGS ON METAL SURFACES

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The production of protective corrosion-resistant coatings on metal surfaces by treatment of the metal with a dilute solution of phosphoric acid or a metal phosphate is well known. Iron or steel and zinc are the metals most commonly treated, and common examples of treating solutions are dilute solutions of phosphoric acid with iron phosphate, manganese phosphate or zinc phosphate. Coatings formed in this way are efficient bonds for organic finishes such as paints, enamels or lacquers and are of considerable commercial importance.

The formation of such coatings involves treating the metal surface with the solution for a period of time which may extend to several hours. Various attempts have been made to reduce this time of treating and thereby increase the efficiency of the process. One such proposal has been the addition to the phosphating bath of phosphates of metals less basic than the metal being treated. For example, copper phosphate may be added to a bath in which iron or steel is being treated and gives a reduction in treating time.

It has now been discovered that remarkable reductions in treating time associated with phosphate coatings of excellent quality may be obtained by the incorporation in the phosphating solution of very small quantities of at least two metals one of which is more basic and the other less basic than the metal being treated. The basicity of metals as used throughout the specification and claims is that given in Mellor's table of the electro-chemical series of metals as given in Mellor's "Comprehensive Treatise on Inorganic and Theoretical Chemistry," volume I, page 1014 (1922 edition).

The present invention accordingly comprises a process for the production of corrosion-resistant coatings on metals or alloys by treatment with an aqueous solution containing the acid radical of phosphoric acid, wherein there are present in the solution small quantities of the cations of at least two metals, one more basic and the other less basic than the metal being treated, the total amount of such cations not exceeding 0.04 gm. per litre of the said aqueous solution.

Since it is generally undesirable to have the anions of mineral acids present in the bath to any significant extent, it is theoretically sounder to add the metals to the bath in the form of their phosphates. Since, however, only extremely small quantities are involved, satisfactory results are obtained in practice using other soluble salts, e. g. chlorides or nitrates.

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While the invention in its simplest form envisages the addition of two metals to the bath, it is found that even better results are obtained by adding three, four or more cationic metals, e. g. one more basic and two less basic; two more basic and one less basic, or two more and two less basic.

It has been found by experiment that the ratios and total amounts of the added metal ions needed to give optimum results are critical for each set of metals as will be shown in more detail later. Although no theoretical explanation has yet been worked out, it seems possible that the added metals may in some way influence the electrode potential of the metal surface under treatment.

To illustrate the process of the invention, the effects of adding various amounts of cationic zinc, cobalt and nickel to a ferrous phosphate concentrate, subsequently diluted twenty-five times to form a treating bath used for the treatment of a steel sheet, are described below.

When keeping the concentration of cobalt and nickel constant at 0.017 and 0.114 gm./litre respectively, it was found that with no zinc present the treating time (shown by the cessation of gassing of the sample) was about 45 minutes, whilst with a zinc concentration of 0.048 gm./litre it dropped to 15 minutes. When the zinc concentration was raised to 0.168 gm./litre, the time increased to 23 minutes, and with a concentration of 0.480 gm. per litre it dropped to 12 minutes. Increasing the zinc concentration above this limit caused a steady increase in the treating time. When treating time is plotted against zinc concentration, the curve shows two distinct minima at the zinc concentrations of 0.048 gm./litre and 0.480 gm./litre mentioned above.

If now the zinc and cobalt concentrations are kept constant at 0.048 gm./litre and 0.017 gm./litre respectively and the nickel concentration is varied, it is found that the treating time with no nickel is erratic and of the order of 1½ hours which is an improvement over the treating time for the plain iron phosphate bath which is 2 hours or more. With 0.074 gm./litre of nickel the time dropped to 18 minutes, 0.19 gm./litre of nickel raised it to 35 minutes, and 0.24 gm./litre of nickel lowered it to 18 minutes again.

Similar tests with cobalt, maintaining zinc and nickel constant at 0.048 and 0.074 gm./litre respectively, gave a time of 35 minutes for no cobalt, 15 minutes for 0.02 gm. cobalt and 34 minutes for 0.07 gm. cobalt per litre.

From the above, it will be seen that optimum results are given with zinc, cobalt and nickel present in concentrations of 0.048, 0.017 and 0.074 gm. per litre respectively. The concentrations in the phosphating bath are 0.00192, 0.00068 and 0.00296 gram per litre respectively. This is roughly equivalent to an atomic ratio of 3:2:6. If the ratio is kept constant, but the amounts are doubled, the processing time increases, which establishes that the phenomenon is a function of the actual concentration of the three metals and not only of their relative proportions.

While no fixed limits can be given, it will be clear that the amounts of metal ions added to the phosphating bath are extremely small, and far less than the amounts of various additives which have been customarily added in the prior art. Thus, when using zinc, cobalt and nickel the total amount of added metal is between 0.10 and 0.15 gm. per litre of concentrate, subsequently diluted twenty-five times to form the phosphating bath, and it seems probable that the total amounts of any metals to be added to the concentrate will be less than 1 gm./litre and probably less than 0.5 gm./litre. In some cases, of course, the maximum concentration of any given metal will be limited by the solubility of its phosphate in phosphoric acid.

A series of experiments were carried out using the molar equivalent of magnesium, aluminium, barium, strontium, manganese, calcium and chromium, as the more basic metals in place of the zinc, in the zinc-cobalt-nickel mixture mentioned above. Similar improvements in treating time were obtained, but it was found that these were not the maximum obtainable when using these alternative metals with cobalt and nickel. Thus, for example, the addition of half the molar equivalent of magnesium was found to be more effective than the addition of the molar equivalent, which in turn was more effective than twice the molar equivalent. In other words, the addition to a litre of concentrate of 0.017 gm. of cobalt, 0.074 gm. of nickel and 0.009 gm. of magnesium was more effective than when the magnesium concentration was increased to 0.018 gm. and further increase to 0.036 gram still further reduced the effect.

It is possible that the optimum relative proportions and absolute concentrations of any particular combination of metallic ions in the solution may be a function of their mobilities or of the ease with which they can be adsorbed by a phosphate layer. Sufficient data is not yet available to substantiate this, however.

Whatever the true explanation of the effect of these very small additions, it can be shown that their effect is due to a different mechanism from that of the much larger amounts of various additions which have been made in the prior art. This is indicated by the loss of the acceleration effect obtained by the addition of larger quantities as already shown in the cases of cobalt, nickel, zinc and magnesium, and is even more strikingly indicated in the case of other metals where the addition of the small amounts quoted has a definite effect in shortening the treating time, whereas addition of amounts of the same metallic ions comparable with those customarily added in the prior art produce a deceleration or even completely inhibit the production of an adherent phosphate layer upon ferrous articles treated in the bath. For example, the addition of 0.00076 gm. of aluminium per litre of treating solution to a solution containing 0.00068 gm. of cobalt and 0.00296 gm. of nickel per litre of treating solution resulted in a reduction in the treating time of 29% of that previously required, whereas the addition of 0.076 gm. of aluminium per litre to the same solution resulted in the complete inhibition of the formation of an adherent phosphate film.

Another series of experiments showed that the analogous substitution of the molar equivalent of ammonium, sodium, or potassium for the zinc was virtually without effect on the treatment time. A slight decrease in treatment time was observed but this was not comparable with that produced by metals forming insoluble phosphates and was of such an order as to be conceivably within the limits of experimental error. The alkali metals are thus excluded from the scope of the present invention.

In order to substantiate the assertion that it is essential to have at least one metal more basic and one less basic than iron present, a series of experiments were carried out to determine the effect of additions of minor quantites of the cations of some of the more basic metals already mentioned. Thus, amounts of the same order as those already referred to, of zinc, calcium, manganese and magnesium were added to a ferrous phosphate bath in varying combinations and ratios. In no case was any significant alteration in the treatment time observed.

The advantages of the invention will be readily apparent from the following examples, in all of which there was employed a bath prepared from a concentrate made by dissolving 150 grams of ferrous phosphate and 15 grams of iron filings in 200 ccs. concentrated phosphoric acid and 800 ccs. of water. This concentrate was diluted to give a bath of 30 points strength, (the points strength is the number of ccs, of decinormal caustic soda needed to neutralise 10 ccs. of the bath solution, using phenolphthalein as an indicator), which was operated at 98° C. Test panels were cut from a single sheet of high lustre cold rolled steel sheet. These test panels were first degreased and then immersed in the bath without further pretreatment.

Example 1.—Standard for comparison

The bath as described above was employed without the addition of any metal additives. The treating time, as measured to the cessation of evolution of hydrogen was 114 minutes.

Example 2

To the concentrate there were added 0.047 gm./litre of cationic zinc and 0.074 gm./litre of cationic nickel. The treating time was reduced to 48 minutes, i. e. only 42% of that required in Example 1.

Example 3

In this case the additions to the concentrate were 0.047 gm./litre of zinc, 0.074 gm./litre of nickel and 0.025 gm./litre of cobalt. The treating time was reduced to 30 minutes, i. e. only 26.2 % of that required in Example 1.

Example 4

To a concentrate as used in Example 3, there was also added 0.018 gm./litre of magnesium. The treating time was 24 minutes, i. e. only 21% of that required in Example 1.

A list of solutions which have been found experimentally to be of great value, giving an average treating time of the order of one third of that needed when no additives are present, is

given below. The standard concentrate described with reference to the examples was used and there are set out the amounts of metal ion to be added to each litre of concentrate. For ease of reference metals more electro-positive than iron are indicated as (+) and those more electro-negative as (−). Total weights of added metal ions are also indicated.

Solution		Grams
A:	0.048 gm. zinc (+)	0.122
	0.074 gm. nickel (−)	
B:	0.048 gm. zinc (+)	0.139
	0.017 gm. cobalt (−)	
	0.074 gm. nickel (−)	
C:	0.009 gm. magnesium (+)	0.100
	0.017 gm. cobalt (−)	
	0.074 gm. nickel (−)	
D:	0.019 gm. aluminium (+)	0.118
	0.025 gm. cobalt (−)	
	0.074 gm. nickel (−)	
E:	0.048 gm. zinc (+)	0.262
	0.175 gm. lead (−)	
	0.0393 gm. copper (−)	
F:	0.0169 gm. zinc (+)	0.0775
	0.0183 gm. nickel (−)	
	0.0030 gm. cobalt (−)	
	0.0393 gm. copper (−)	
G:	0.098 gm. barium (+)	0.197
	0.074 gm. nickel (−)	
	0.025 gm. cobalt (−)	
H:	0.063 gm. strontium (+)	0.154
	0.017 gm. cobalt (−)	
	0.074 gm. nickel (−)	
I:	0.029 gm. calcium (+)	0.120
	0.017 gm. cobalt (−)	
	0.074 gm. nickel (−)	
J:	0.018 gm. magnesium (+)	0.232
	0.175 gm. lead (−)	
	0.0393 gm. copper (−)	
K:	0.041 gm. manganese (+)	0.140
	0.025 gm. cobalt (−)	
	0.074 gm. nickel (−)	
L:	0.039 gm. chromium (+)	0.130
	0.017 gm. cobalt (−)	
	0.074 gm. nickel (−)	
M:	0.047 gm. zinc (+)	0.175
	0.029 gm. calcium (+)	
	0.074 gm. nickel (−)	
	0.025 gm. cobalt (−)	
N:	0.048 gm. zinc (+)	0.165
	0.018 gm. magnesium (+)	
	0.074 gm. nickel (−)	
	0.025 gm. cobalt (−)	

From the foregoing it will be seen that the preferred range of added metal ion concentrations in the concentrate is from about 0.075 to about 0.25 gm. per litre, the corresponding bath concentrations being about one twenty-fifth as much, i. e. from 0.003 to 0.01 gm. per litre. The upper limit in the concentrate is considered to be 1 gm./litre, and preferably the concentration

is less than 0.5 gm./litre, the corresponding bath concentrations being 0.04 and 0.02 gm./litre.

Apart from the fact that alkali metals are ineffective and therefore outside the scope of the invention, there are a few other elementary factors which should be considered. Thus materials which would precipitate some or all of the added metals should be absent from the bath. Thus, copper or other metals in group II of the qualitative analysis table should not be used with a phosphating bath containing hydrogen sulphide.

The invention also includes phosphating baths for use in the process, such baths containing the acid radical of phosphoric acid and the metal cations as previously described. The bath strength is desirable 30 points, but a margin of 4 or 5 points either way is permissible. Other bath strengths may however be used, as is known in the art, in which case the additions to the concentrate are adjusted to maintain the total amounts of added metal in the treating solution within the limits specified herein. In the concentrates the relative proportions of the ingredients will obviously be the same as in the bath, the conventional degree of concentration being 25 times as already stated. Other degrees of concentration are obviously possible.

Furthermore, although the invention has been described with reference to a ferrous phosphate bath, good results were obtained with zinc phosphate baths and manganese phosphate baths which are commonly used alternatives. Thus the addition of alkaline earth metals, especially calcium, together with cobalt and nickel (cf. solution I) to a zinc phosphate bath was found most effective.

I claim:

1. A process for the production of corrosion-resistant coatings on a metal selected from the group which consists of zinc and iron, which comprises treating said metal in an aqueous solution which contains essentially at least one primary orthophosphate of a metal selected from the group which consists of zinc, manganese and iron, there being also present in said aqueous solution at least a very small amount of the cations of at least two metals, neither of said metals being an alkali metal and one of said metals being more basic than the metal being treated, and the other of said metals being less basic than the metal being treated, the total amount of said cations present in said solution ranging from 0.003 to about 0.04 gram per litre of the said aqueous solution, said cations being present as part of a water-soluble salt of said metals, or as substances which form water-soluble acid phosphates.

2. A process for the production of corrosion-resistant coatings on metal as defined in claim 1, wherein the total amount of said cations present in said aqueous solution does not exceed 0.02 gram per litre of said aqueous solution.

3. A process as defined in claim 1, wherein the total amount of said cations present in said aqueous solution ranges from 0.003 gram to 0.01 gram per litre of said aqueous solution.

4. A process for the production of corrosion-resistant coatings on metal as defined in claim 1, wherein the metal being treated is a ferrous metal and the primary orthophosphate is ferrous orthophosphate, the more basic metal includes at least one metal selected from the group which consists of zinc, magnesium, aluminum, barium, strontium, manganese, calcium, and chromium, and the less basic metal includes at least one

metal selected from the group which consists of nickel, cobalt, lead and copper.

5. An improved phosphating bath for the treatment of metallic surfaces; comprising an aqueous solution containing essentially at least one primary metal orthophosphate of a metal selected from the group which consists of zinc, manganese and iron, said solution containing at least a very small amount of the cations of at least two metals other than alkali metals, one of said two metals being more basic and the other less basic than a metal selected from the group consisting of iron and zinc, the total amounts of said cations being comprised within a range extending from 0.003 gram per litre to 0.04 gram per litre of said aqueous solution, said cations being present as ionic constituents of salts which are soluble in said aqueous solution.

6. An improved phosphating bath as defined in claim 5, wherein the total amount of said cations present does not exceed 0.02 gram per litre of bath solution.

7. An improved phosphating bath as defined in claim 5, wherein the total amount of said cations of said two metals does not exceed 0.01 gram per litre of bath solution.

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