BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1555—1558 (1969)

Influence of Impurities on Phosphate Coating Formation[*1]

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(Received October 5, 1968)

The applicability of wet-process phosphoric acid containing such impurities as Al^{3+}, Ca^{2+}, Fe^{3+} and SO_4^{2-} was examined. From the viewpoint of the corrosion resistivity of the phosphate coating, Al^{3+} ion was found to be the most undesirable contaminator. NaF was recognized as the most effective masking reagent for an elimination of Al^{3+} hindrance. SO_4^{2-} also affected the phosphate coating formation, but the presence of less than 1% SO_4^{2-} did not disturb the coating formation when an appropriate amount of accelerator was added to the phosphatizing solution.

This investigation was initiated for the purpose of examining whether phosphoric acid manufactured by wet-process was applicable to a process of phosphate coating or not. Recently, a wet-process phosphoric acid has come to be available at cheap cost in Japan. In ordinary methods, however, it is impossible to use phosphoric acid as raw material for the phosphatizing solution because of the presence of such impurities as Al^{3+}, Ca^{2+}, SO_4^{2-} and so on. Khain[1-4] has already investigated the formation of the phosphate coating, using the phosphatizing solution containing nitrates of metals with mono-, bi- and trivalency as reaction accelerators. As the pH lowering occured in their solutions, characteristic effect of nitrates could not be examined individually. The qualitative study of undesirable influences of SO_4^{2-}, AsO_4^{3-}, Cr^{3+} and Al^{3+} in the ordinary acidic bath of zinc phosphate was also reported by Nagai.[5] In the present paper influences of Al^{3+}, Fe^{3+}, Ca^{2+} and SO_4^{2-} on $Zn_3(PO_4)_2$ phosphatizing solutions were described, and an effective chemical procedure was proposed to eliminate the hindrance of Al^{3+}.

Experimental

A) Stock Solution for Phosphatization. A solution was prepared by dissolving 17 g of zinc oxide in 34 g of boiling 85% phosphoric acid, cooled to room temperature, and then adding 6 g of 60% nitric acid, diluted finally to 100 m*l* with distilled water. All chemicals used were reagent-grade materials. Table 1 shows the composition of the solution thus prepared.

Table 1. Composition of stock solution for phosphating (wt%)

Zn^{2+}	PO_4^{3-}	NO_3^-
10.3	24.8	4.34

B) Phosphatizing Solution. Various kinds of phosphatizing solutions were prepared by adding 1.7 g of Na_2CO_3 and a certain amount of 18% $NaNO_2$ solution as an accelerator to 95 g of the above-mentioned stock solution, and diluting to 1*l* with distilled water. At this stage, free acidity and total acidity of the solution were 1.98 and 30.56 in point,[*3] respectively. Furthermore, SO_4^{2-}, NO_3^-, Al^{3+}, Ca^{2+} and Fe^{3+} were added to the above solutions for experiments on the effects of these materials.

C) Procedure. Specimens of commercial mild steel, 3 mm × 5 mm × 20 mm, were used for the phosphate coating. The elemental composition of the mild steel is given in Table 2. The specimens were polished with emery paper (No. 400), degreased with benzene, dried, and dipped into the phosphatizing solution. After phosphatization at 25°C, the amount of iron dissolved from the specimen in the solution was determined by colorimetric analysis with Nitroso R salt. The corrosion resistance of phosphate coating was tested by dipping the specimen in a 100 m*l* of air-bubbled 3% NaCl solution for 10 hr at 25°C and then determining the amount of iron dissolved in the solution. A relative resistivity of phosphate coating may be indicated by this test, although it has not been officially approved yet.

Table 2. Composition of mild steel used (wt%)

C	Si	Mn	P	S	Cu	Cr	Ni
0.13	trace	0.53	0.03	0.026	0.05	trace	trace

[*1] Presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

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1) I. I. Khain, *J. Appl. Chem. USSR.*, **32**, 2531 (1959).

2) I. I. Khain, *ibid.*, **32**, 2542 (1959).

3) I. I. Khain, *ibid.*, **32**, 2662 (1959).

4) I. I. Khain, *ibid.*, **32**, 1481 (1959).

5) Y. Nagai, *Kinzoku Hyomen Gijutsu (J. Metal Finishing Soc. Japan)*, **12**, 7, 253 (1961).

[*3] Point is equal to m*l* of 0.1 N NaOH which is required to titrate 10 m*l* of a phosphatizing solution. Total acidity represents the the titer of 0.1 N NaOH when phenolphthalein is used as an indicator. Free acidity is equal to the titer of 0.1 N NaOH in case of bromophenol blue.

Results and Discussion

The experimental results at various concentrations of accelerators are shown in Figs. 1 and 2. The amount of dissolved iron increased linearly with phosphatizing time, in the case of the solution containing 1 g/*l* of the accelerator concentration as shown in Fig. 1, whereas, at 2g/*l* and 3 g/*l* of the accelerator concentration, the amount of dissolved iron reached saturation after 20 min. Figure 2 shows that, with respect to the corrosion resistance of phosphate coating, the most favorable concentration of accelerator was 4 g/*l*. The influences of sulfate addition to the phosphatizing solution are shown in Figs. 3 and 4. Sulfate ion caused an increase in amounts of dissolved iron and a decrease of resistivity. The presence of more than 1% sulfate was undesirable in the process of the phosphate coating. Figures 5 and 6 show that the amount of dissolved iron and the corrosion resistance were dependent on the concentration of accelerator when the phosphatizing solution contained 1% of sulfate ion. From the results shown in Fig. 6, it was concluded that the presence of 1% sulfate ion did not disturb the film formation if more than 4 g/*l* of the accelerator was added to the phosphatizing solution. As shown in Fig. 7, the lessening of corrosion resistivity was caused by addition of $Al(NO_3)_3$ and $Fe(NO_3)_3$, whereas the phosphatizing solution containing 3—5 g/*l* of

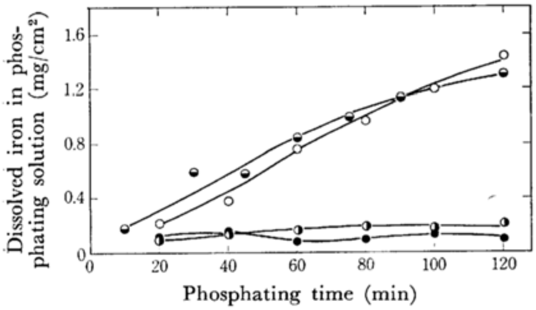

Fig. 1. Variation of amount of dissolved iron in phosphatizing solution with phosphatizing time at various concentrations of accelerator.
Accelerator concn. —◒—: 1 g/*l*, —○—: 2 g/*l*, —◑—: 4 g/*l*, —●—: 8 g/*l*

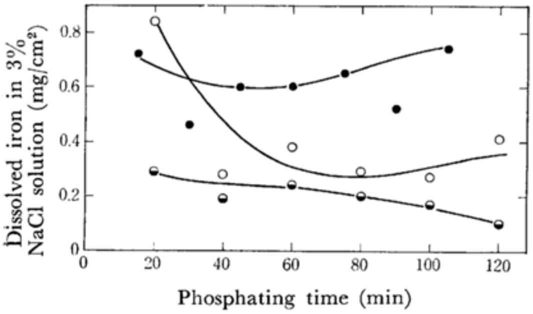

Fig. 2. Variation of relative resistivity with phosphating time at various concentrations of accelerator.
accelerator concn. —●—: 1 g/*l*, —○—: 2 g/*l*, —◒—: 4 g/*l*

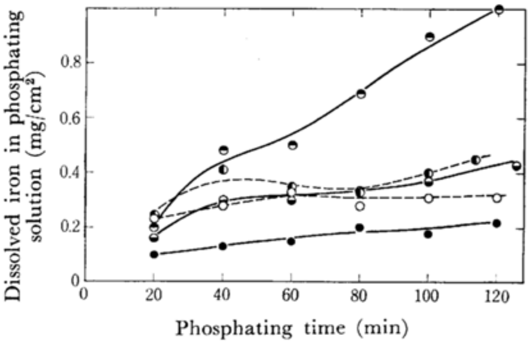

Fig. 3. Variation of amount of dissolved iron in phosphating solution with phosphating time at various concentrations of SO_4^{2-} ion.
SO_4^{2-} concn. —◓—: 3%, - -◐- -: 1.0%, —◒—: 0.6%, - -○- -: 0.3%, —●—: 0%.

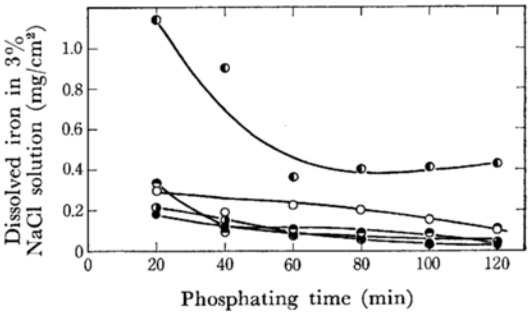

Fig. 4. Variation of relative resistivity with phosphating time at various concentrations of SO_4^{2-} ion.
concn. SO_4^{2-} —◐—: 3.0%, —○—: 1.0%, —●—: 0.6%, —◓—: 0.3%, —◑—: 0%

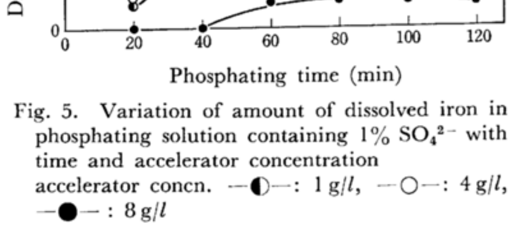

Fig. 5. Variation of amount of dissolved iron in phosphating solution containing 1% SO_4^{2-} with time and accelerator concentration
accelerator concn. —◐—: 1 g/*l*, —○—: 4 g/*l*, —●— : 8 g/*l*

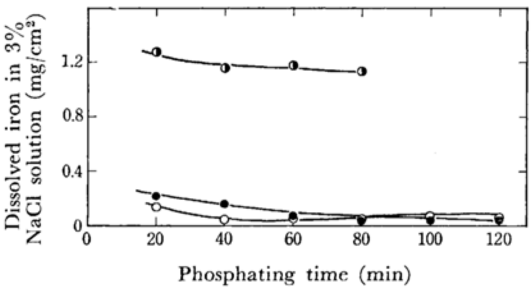

Fig. 6. Variation of relative resistivity with phosphating time at various concentrations of accelerator in case of the addition of 1% SO_4^{2-}. accelerator concn. —◑—: 1 g/*l*, —●—: 4 g/*l*, —○—: 8 g/*l*

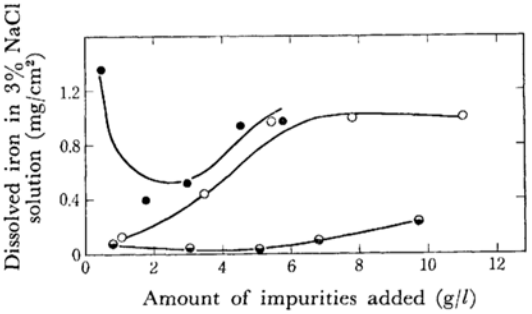

Fig. 7. Variation of relative resistivity with concentration of various impurities.
●: Al^{3+}, ○: Fe^{3+}, ◒: Ca^{2+}

$Ca(NO_3)_2$ gave more sturdy film. Fe^{3+} ion does not exist in the phosphatizing solution with high pH, and therefore the influence of Fe^{3+} ion could be easily eliminated by adding alkaline to enhance the pH of the phosphatizing solution. On the other hand, Al^{3+} was recognized as one of the most undesirable contaminators on the phosphatizing solution, because a milky-white amorphous coating lacking in adhesive ability to iron surface appeared by the addition of only 0.585 g/*l* of Al^{3+} and the solution containing 1.76 g/*l* of Al^{3+} gave neither amorphous coating nor oxide film. The maximum allowable concentration of Al^{3+} in the phosphatizing solution was estimated to be less than 0.01 g/*l*. Therefore, various kinds of Al^{3+} masking reagents were examined in order to avoid the Al^{3+} hindrance. Table 3 and Table 4. shown that the corrosion resistivity of the phosphate coating was improved by an addition of NaF, and that the masking effect of NaF was most remarkable. A sturdy coating was obtained by the addition of more than 2 g/*l* of NaF, even though the phosphatizing solution contained 2.93 g/*l* of Al^{3+}. In the case of the presence of 0.23 g/*l* of Al^{3+}, the addition of more than 1.3 g/*l* of NaF to the phosphatizing solution was necessitated. The sturdiness of phosphate coating thus obtained was comparable with that obtained from an ordinary phosphatizing solution without Al^{3+}.

TABLE 3. EFFECT OF Al^{3+} MASKING REAGENTS

Masking reagents	Reagent concn. g/*l*	Al^{3+} concn. g/*l*	Dissolved iron in 30% NaCl soln. (mg/cm²)
NaF	2.50	2.93	0.578
$(NaPO_3)_6$	2.59	2.93	0.699
$Na_4P_2O_7 \cdot 10H_2O$	2.45	2.93	1.49
$KNaC_4H_4O_6 \cdot 4H_2O$	2.75	2.93	1.05
$Na_2C_4H_4O_6 \cdot 6H_2O$	2.79	2.93	0.867
$Na_2C_6H_5O_7 \cdot 2H_2O$	2.60	2.93	0.691
$(NaPO_3)_6$	2.50	0.23	0.850
$Na_4P_2O_7 \cdot 10H_2O$	2.50	0.23	0.831
$KNaC_4H_4O_6 \cdot 4H_2O$	2.50	0.23	1.02
$Na_2C_4H_4O_6 \cdot 6H_2O$	2.50	0.23	0.197
$Na_2C_6H_5O_7 \cdot 2H_2O$	2.50	0.23	0.732

TABLE 4. MASKING EFFECT OF NaF

NaF concn. g/*l*	Al^{3+} concn. g/*l*	Dissolved iron in 3% NaCl soln. (mg/cm²)
0.42	2.93	0.920
1.26	2.93	0.976
1.68	2.93	0.125
2.10	2.93	0.123
2.94	2.93	0.075
4.62	2.93	0.031
0.43	0.23	0.933
1.28	0.23	0.058
2.13	0.23	0.043
3.05	0.23	0.074
3.83	0.23	0.010
4.68	0.23	0.023

Conclusion

The reaction mechanism of phosphate coating formation is commonly accepted as follows:

$$(1)\quad Fe + 2H_3PO_4 = Fe(H_2PO_4)_2 + H_2$$

$$(2)\quad Zn(H_2PO_4)_2 = ZnHPO_4 + H_3PO_4$$

$$(3)\quad ZnHPO_4 = Zn_3(PO_4)_2 + H_3PO_4$$

Corrosion reaction represented by Eq. (1) begins when the iron specimen is dipped in the phosphatizing solution. As a result, both equilibriums of Eq. (2) and (3) are shifted to the right hand by the decrease of H_3PO_4 concentration and then an insoluble $Zn_3(PO_4)_2$ crystallized on the iron surface. Recently, composition and crystal structure of the phosphate coating have been classified by many investigators. Therefore, in addition to the abovementioned qualitative explanation, the rate-determining factors of the coating formation can be discussed, taking the precise crystal structure into consideration. Later, the hindrance of Al^{3+} and the reaction mechanism will be reported, from a viewpoint of electrochemistry. Although a theoretical explanation of the influence of each impurity has not been established yet, the following conclusions have been made: (a) Al^{3+} is the most undesirable contaminator for the phosphatizing solution, and the addition of NaF is effective in eliminating the hindrance of Al^{3+}. (b) The interference of Fe^{3+} can be avoided by the addition of alkali to the phosphatizing solution. (c) The addition of an appropriate amount of the accelerator makes it possible to use the wet-process phosphoric acid containing Ca^{2+} and SO_4^{2-} as raw material for the phosphatizing solution.

This investigation was supported by a grant from Nippon Kokan (Japan Steel and Tube) Corp., for which the authors wish to express their sincere appreciation.