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Ultrasonic Effect on Phosphate Coating Formation*[1]

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The recent development of high power generators of ultrasonic wave has broadened its scope of application. If it is applied to the phosphatizing process, the cavitation caused by ultrasonic radiation in the phosphatizing solution is expected to prevent passivation of iron, and, removing hydrogen gas from the iron surface, to bring about a stirring effect. Ultrasonic cavitation is considered to eliminate the hindrance of Al^{3+} which has been recognized as one of the most undesirable contaminators when wet-process phosphoric acid is used as raw material for phosphatizing solution.[1] A few investigations of the ultrasonic effects[2-4] on the phosphate coating have been already reported, but the pH range of the phosphatizing solution and the condition of radiation for these investigations are limited. The present investigation has been undertaken to obtain the optimum condition for the formation of the phosphate coating under ultrasonic radiation.

Experimental

A) Phophatizing Solution. The phosphatizing solution was prepared by diluting phosphoric acid and dissolving a certain amount of $NaNO_3$, Na_2CO_3 and $Zn_3(PO_4)_2$. Differing from a commercial phosphatizing solution, the solution used in this experiment contained a large amount of zinc phosphate precipitates. The relationship between Na_2CO_3 and H_3PO_4 is shown in Fig. 1. The concentrations of $NaNO_3$ and $Zn_3(PO_4)_2 \cdot 4H_2O$ were fixed at 3.3 g/*l* and 19.3 g/*l*, respectively. The pH of the solution, as shown in Fig. 1 varied largely with the composition of the solution.

B) Apparatus and Procedure for Measurement. The apparatus consisted of a high frequency oscillator of alternate current and several magneto-restriction vibrators. The frequency of ultrasonic wave was altered by changing magneto-restriction vibrators within the range from 16 kc to 100 kc. The intensity of ultrasonic wave was continuously changeable from 0 W to 500 W. A polyethylene beaker containing the phosphatizing solution was placed on the radiation plane of the vibrator and a metal specimen was suspended with nylon fiber in the solution. The apparatus is schematically show in Fig. 2. Before the phosphatization the specimens were treated by the method describ-

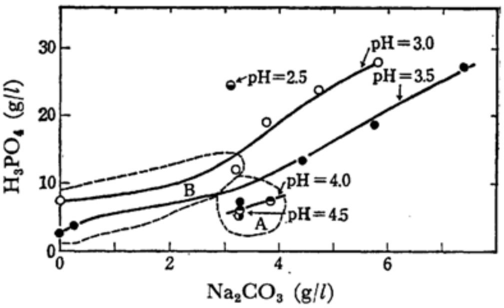

Fig. 1. Relationship among concentrations of H_3PO_4 and Na_2CO_3 and pH's of phosphatizing solutions.

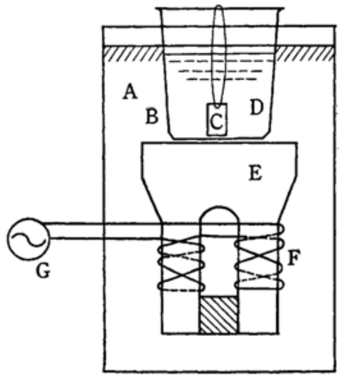

Fig. 2. Apparatus for ultrasonic radiation.
A. thermostatic bath, B. polyethylene-made beaker, C. specimen, D. phosphatizing solution, E. magneto-restriction vibrator, F. exciting coil, G. ultrasonic oscillator

TABLE 1. COMPOSITION OF MILD STEEL USED

C	Si	Mn	P
0.20	trace	0.80	0.016

S	Cu	Cr	Ni
0.024	0.06	0.06	0.03

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[1] T. Umegaki, H. Ito and T. Okabe, This Bulletin, **42**, 1555 (1969).

[2] L. E. C. Gandil, Brit. Pat. 885686 (1961).

[3] T. Kataoka, Japanese Pat. 8509 (1958).

[4] A. M. Ginberg and M. A. Naishuller, *J. Appl. Chem. USSR*, **37**, 551 (1964).

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ed in a previous paper.[1] The composition of the specimens is shown in Table 1.

C) Amount of Phosphate Film. The weight of the coating was estimated by measuring the weight change of the specimens by dipping in a stripping solution containing 20% of CrO_3.

D) Corrosion Test. The corrosion resistivity of the phosphate coating was tested in the same manner as described in the preceding paper.[1] In this test the dipping time was cut to 5 hr, whereas the ten-hour test has been adopted previously.

Results and Discussion

The optimum composition of the phosphatizing solution under radiation of ultrasonic wave was sought at 50°C by microscopic observation on the phosphate coating. All experiments were done under radiation of ultrasonic wave with a frequency of 20 kc and an intensity of 25 W/cm². This ultrasonic radiation was adopted, taking the stability and feasibility in the generation of ultrasonic wave into consideration. As a preliminary experiment, commercial phosphatizing solutions were used for

TABLE 2. RELATIONSHIP BETWEEN COATING WEIGHT AND THE COMPOSITION OF PHOSPHATING SOLUTION

Phosphating soln. No.	pH	H_3PO_4 (g/l)	Na_2CO_3 (g/l)	Coating weight (mg·cm²)
1	2.5	24.5	3.11	—
2	3.0	7.79	0.00	0.23
3	3.0	12.1	3.23	0.26
4	3.0	19.0	3.77	—
5	3.0	23.8	4.73	—
6	3.0	28.2	5.84	—
7	3.5	2.90	0.00	0.38
8	3.5	3.85	0.25	0.17
9	3.5	7.79	3.30	0.34
10	3.5	13.3	4.45	0.17
11	3.5	18.6	5.77	0.05
12	3.5	27.6	7.39	0.10
13	4.0	6.34	3.30	0.09
14	4.0	7.79	3.85	0.11
15	4.5	6.04	3.30	0.11

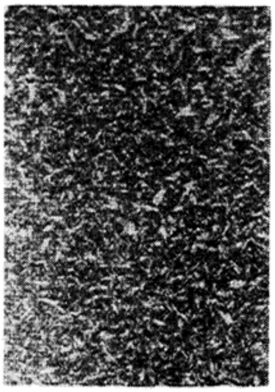

Fig. 3. Phosphate coating from the solution belonging to region B.
(5 min) (×180)

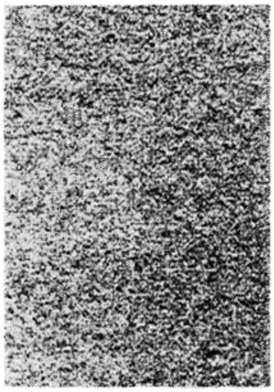

Fig. 4. Phosphate coating from the solution belonging to region A.
(5 min) (×180)

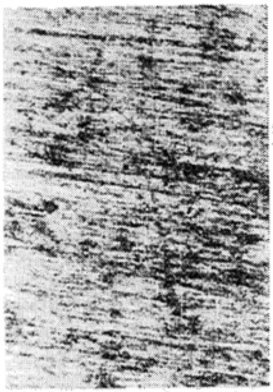

Fig. 5. Typical coating from the phosphating solutions of Nos. 10, 11, 12 and 14.
(5 min) (×180)

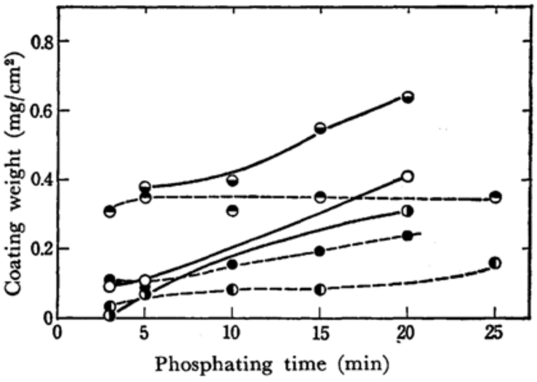

Fig. 6. Variation of coating weight with phosphating time at 50°C.

◓ ◒ } soln. No. 9 ○ ● } soln. No. 13

◐ ◑ } soln. No. 15

solid line: ultrasonic radiation
broken line: without radiation

phosphatization. So far as the microscopic observation on the phosphate coating showed, under ultrasonic radiation, no excellent coating was obtained in these solutions with considerably low pH. In the course of experiments under ultrasonic radiation, however, a slurry solution containing insoluble zinc phosphate was found to give a thin but sturdy coating. The relationship between the weight of the phosphate coating and the composition of the phosphatizing solution is shown in Table 2. At high concentration of H_3PO_4 and at low concentration of Na_2CO_3, a bulky and coarse coating was obtained. The solution which belonged to region B of Fig. 1 gave a coating such as shown in Fig. 3. Figure 4 shows the typical coating produced in the solution belonging to region A in Fig. 1. Compared with the solution in region B, the solution in region A gave thin coating, and the specimen used was uniformly covered with fine crystals. As shown in Fig. 5, a uniform coating was not obtained in the phosphatizing solutions of Nos. 10, 11, 12 and 14 listed in Table 1, the compositions of which belonged to neither of those in region A nor in region B. From microscopic observation of the coating surfaces, the solution region A was assumed to have the optimum composition under ultrasonic radiation. The optimum

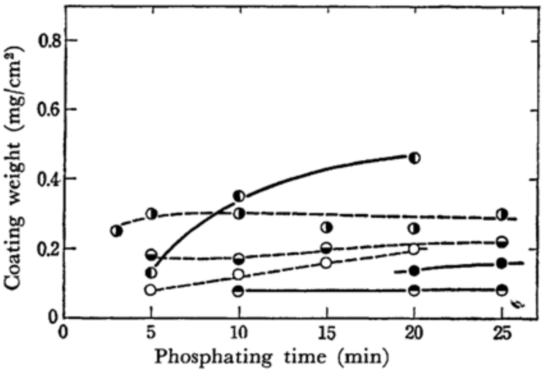

Fig. 7. Variation of coating weight with phosphating time at 75°C.

◐ ◑ } soln. No. 9 ◓ ◒ } soln. No. 13

○ ● } soln. No. 15

solid line: ultrasonic radiation

broken line: without radiation

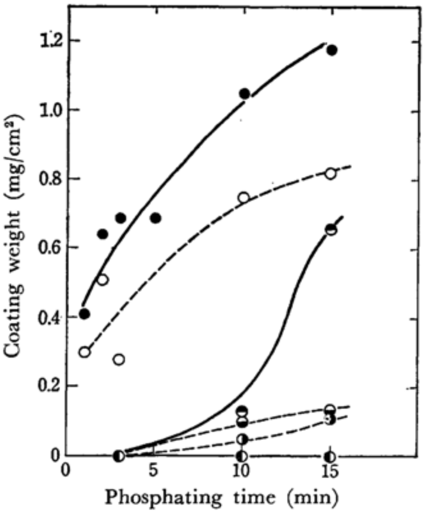

Fig. 8. Variation of coating weight with phosphating time at 95°C.

● ○ } soln. No. 9 ◓ ◒ } soln. No. 13

◑ ◐ } soln. No. 15

solid line: ultrasonic radiation

broken line: without radiation

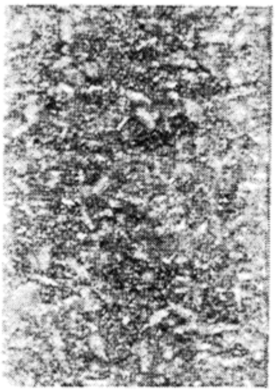

Fig. 9. Phosphate coating under ultrasonic radiation 95°C. (5 min) (×180)

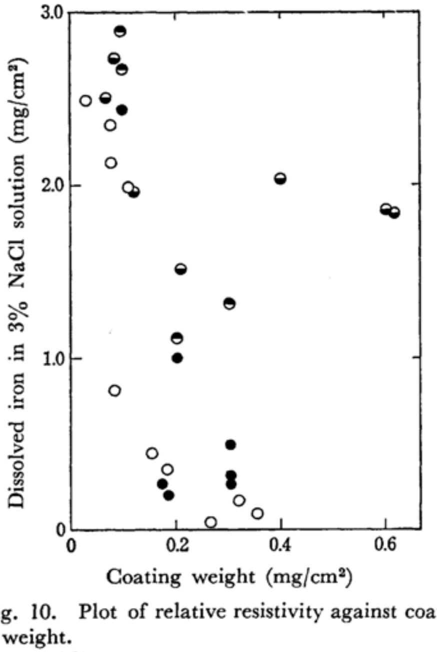

Fig. 10. Plot of relative resistivity against coating weight.

● 50°C ○ 75°C } ultrasonic radiation

◓ 50°C ◒ 75°C } without radiation

pH range of the solution of the phosphatizing process under ultrasonic radiation is 3—4, which is favorable for the precipitation of Al^{3+} and the elimination of its hindrance. The changes of the coating weight with the duration of phosphatization at 50, 75 and 95°C are shown in Figs. 6, 7 and 8. Figures 6 and 7 indicate that, under ultrasonic radiation, the saturation of the coating weight was present in the phosphatizing process, whereas the coating weight without radiation of ultrasonic wave increased gradually with time. The coating surface obtained at 95°C, in spite of its large thickness, was coarse and deficient in uniformity as shown in Fig. 9. On the other hand, the coatings obtained at 50 and 75°C were thin but sturdy. In Fig. 10, the amount of dissolved iron indicating the relative resistivity of coating, in the air-bubbled 3% NaCl solution, is plotted against the coating weight. The coating obtained under radiation of ultrasonic wave was found to be more sturdy than that treated by the ordinary dipping method, as is shown in Fig. 10. Figures 11 and 12 show the films obtained on the surfaces which had been oxidized by concentrated HNO_3 before phosphatization. In spite of the presence of oxide film on the specimen, a uniform film, shown in Fig. 11 was obtained by ultrasonic radiation. From comparison of Fig. 13 with Fig. 14, it has been revealed that ultrasonic wave also facilitated the film formation on the surface stained with mineral oil.

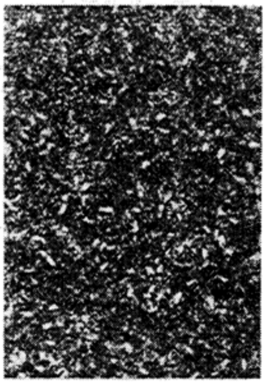

Fig. 11. Phosphate coating on oxide-covered surface under ultrasonic radiation. (5 min) (×180)

Fig. 12. Phosphate coating on oxide-covered surface without ultrasonic radiation. (5 min) (×180)

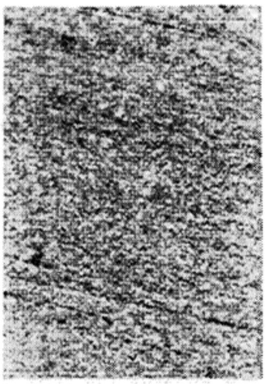

Fig. 13. Phosphate coating on oil-stained surface under ultrasonic radiation. (5 min) (×180)

Fig. 14. Phosphate coating on oil-stained surface. without ultrasonic radiation. (5 min) (×180)

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