Properties of Protective Films Formed on an Iron Surface by Dialkyl Phosphate as a Corrosion Inhibitor

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The properties of films formed on an iron surface by di-*n*-dodecyl phosphate were studied. The inhibition effects for iron specimens treated with dodecyl phosphate were estimated from the losses in weight of iron specimens in 5% NaCl aqueous solutions. The Fe L_α, L_β X-ray emission spectra of the iron surface were obtained by electron microprobe X-ray analysis. The value of the intensity ratio, Fe L_β/L_α, of the untreated iron specimen was 0.17, while that of the treated iron specimen was 0.28. The infrared spectrum of the treated iron surface was similar to that of tribasic orthophosphate. The content of Fe in the film formed on the iron surface by di-*n*-dodecyl phosphate was from 4.3% to 6.98%. From these results, it was inferred that di-*n*-dodecyl phosphate reacted with iron atoms at the iron surface in a cyclohexane solution and that the main component of the film formed on the iron surface was $[(RO)_2POO]_2Fe$ or $[(RO)_2POO]_3Fe$.

Corrosion inhibitors for recirculating cooling water are grouped into three classes—that is, inhibitors which passivate the metal surface, those which precipitate on the metal surface, and those which are adsorbed on the metal surface, by the formation mechanism of the film on the metal surface.[1] It is thought[2] that dialkyl phosphate is adsorbed on an iron surface with the orthophosphate ion, but the mechanism of film formation by dialkyl phosphate has not yet been studied in detail. In this paper, the properties of the films formed on an iron surface by di-*n*-dodecyl phosphate $(C_{12}H_{25}O)_2PO(OH)$ were studied by measurements of the Fe L_α, and L_β X-ray emission spectra, the infrared spectra, and the contents of the film formed on the iron surface.

Experimental

Materials. The iron specimens used were the same as those used in the previous work.[3] The di-*n*-dodecyl phosphate was synthesized by a known procedure[4] and was purified by recrystallization. No significant impurities were detected in the mass spectrum of the di-*n*-dodecyl phosphate used in these experiments.

Procedures. Iron specimens were placed in C_6H_{12}, CCl_4 and $CHCl_3$ solutions of dodecyl phosphate at 35 °C; then they were taken out of the solutions, washed in the solvent, and wiped with gauze. The inhibition effects of dodecyl phosphate on iron specimens were estimated from the losses in weight of the iron specimens (55×15×0.7 mm) in 5% NaCl aqueous solutions (15 ml) during 24 hr at 35 °C and from the percentage of the rusted surface as estimated by a visual observation of the iron specimens (30×80×1.0 mm) after a humidity test at 40 °C and 95% RH for 48 hr. The Fe L_α, and L_β spectra of the surfaces of iron specimens (10×10×1.0 mm) were measured by means of a Shimadzu-ARL electron microprobe X-ray analyzer EMX-SM with RAP crystals. When the iron specimens were placed in a C_6H_{12} solution of dodecyl phosphate at 35 °C for 7 days, a viscous liquid material adhered to the iron surface. Therefore, the iron specimens were taken out of the solution, as they were, and were placed in a desiccator without washing and wiping; they were then dried at room temperature in the evacuated desiccator. A white film was thereupon separated from the iron surface. The infrared spectra of these films were measured by the tablet method with KBr, and the contents of Fe and P in the C_6H_{12} solutions dissolved from these films were determined by fluorescent X-ray analysis. The preparation of the sample for the analysis was carried out as follows; 200 μl of a solution was dropped onto the miller film and then evaporated to dryness by using an infrared lamp. The intensity of Fe K_α was measured at 57.50° with an LiF crystal and a Cr target, while that of P K_α was measured at 141.05° with a Ge crystal and a Cr target. The infrared spectra of the surfaces of iron specimens (19×56×1.0 mm and 19×47×1.0 mm) treated with dodecyl phosphate were measured by the ATR method.

Results and Discussion

*Inhibition Effects of di-*n*-Dodecyl Phosphate.* The inhibition efficiencies of dodecyl phosphate, as estimated from the losses in weight of the iron specimens and from visual observations of the iron surface, are shown in Table 1. The inhibition effects on iron specimens treated in C_6H_{12} solutions of dodecyl phosphate were more than those on iron specimens treated in other solutions. On the basis of these data, subsequent experiments were carried out in the cyclohexane solutions.

TABLE 1. THE EFFECTS OF SOLVENTS ON THE INHIBITION EFFICIENCIES OF DI-*n*-DODECYL PHOSPHATE FOR IRON SPECIMENS

Solvent[a]	Percent inhibition[b] %	Rusted surface[c] %
C_6H_{12}	66	10
CCl_4	33	70
$CHCl_3$	0	100

a) Concentration of inhibitor is 0.5%. b) By total immersion tests in test tube (15×110 mm, in aerated 5% NaCl solution) at 35 °C for 24 hr. c) By humidity tests in desiccator at 40 °C and 95% RH for 48 hr.

Adsorption-Time Curve of the Dodecyl Phosphate for Iron. The intensity of the P K_α line of the iron surface treated with dodecyl phosphate, as measured by fluorescent X-ray analysis, was introduced instead of the amount of dodecyl phosphate adsorbed on the iron surface. The P K_α intensities of the iron surface are plotted as a function of the time in Fig. 1. The P K_α intensity of the iron surface reached a maximum after 7 days. Therefore, subsequent experiments were carried out by treating the surface fors 7 days; the concentration was 0.5%.

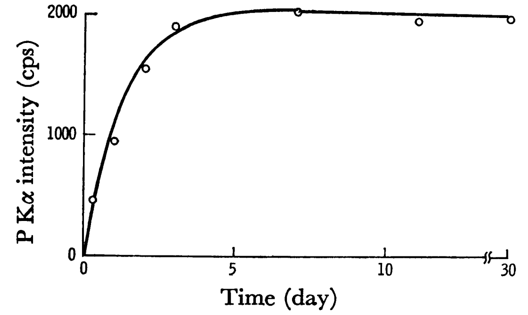

Fig. 1. Adsorption-time curve of di-*n*-dodecyl phosphate for iron specimen, in 0.5% cyclohexane solution at 35 °C.

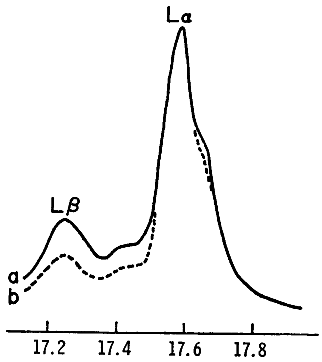

Fig. 2. Fe $L\alpha$, $L\beta$ band spectra for iron specimens.
(a) Iron specimen treated with di-*n*-dodecyl phosphate,
(b) non treated iron specimen.

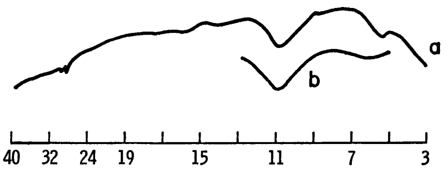

Fig. 3. IR spectra of iron treated with di-*n*-dodecyl phosphate by ATR method (a) and phosphating steel by Sato (b).

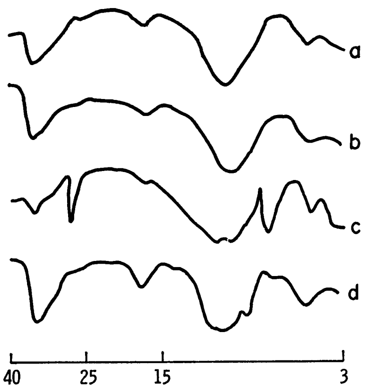

Fig. 4. IR spectra of the products obtained by precipitation reactions of $FeCl_3$ with NaH_2PO_4 (a), Na_2HPO_4 (b), NaH_2PO_4 (c) and $Na_4P_2O_7$ (d).

Fe L_α and L_β X-Ray Emission Spectra of an Iron Surface. The Fe L_α and L_β spectra of an untreated iron surface and a treated iron surface are shown in Fig. 2. These spectra differ from one another in the Fe L_β/L_α intensity ratio. This intensity ratio varies with the Fe-oxidation state.[5] For example,[6] the Fe L_β/L_α intensity ratio of Fe-metal is 0.17, while that of Fe-oxide (Fe_3O_4) is 0.51. The spectra in Fig. 2 show that the ratio for the untreated iron surface is 0.17, while the ratio for the treated iron surface is 0.28. The ratio varies not only with the Fe-oxidation state, but also with the self-absorption effect or with the absorption effects of elements in the film on the surface. The spectra in Fig. 2 were obtained under the same conditions at 10 kV and 0.04 μA, so the self-absorption effect is negligible. The value of the ratio for an iron surface is obtained as only 0.18 instead of 0.17 by the correction of the absorption effects of the components in the film on the iron surface, carbon, oxygen, and phosphorus atoms in dodecyl phosphate. Therefore, the increase in the ratio observed in this experiment shows that the chemical state of the iron atom at the surface is made to vary by the treatment with dodecyl phosphate.

Infrared Spectra. The infrared spectrum of the surface of an iron specimen treated with dodecyl phosphate, as obtained by the ATR method, is shown in Fig. 3, together with the spectrum of the surface of phosphating steel obtained by Sato.[7] Both spectra show broad peaks at about 1100 cm^{-1}. The infrared spectra of the products obtained by the precipitation reactions of ferric chloride with monosodium phosphate, disodium phosphate, sodium hypophosphite, or sodium pyrophosphate are shown in Fig. 4. The spectrum (a) in Fig. 3 is similar to the (a) and (b) spectra in Fig. 4—that is, the spectra of orthophosphate. The spectra of tribasic, dibasic and monobasic orthophosphate were reported by Miller and Wilkins.[8] The (a) spectrum in Fig. 3 is similar to the spectrum of tribasic orthophosphate, which has no OH group. The infrared spectrum of a white film separated from the iron surface, as obtained by the tablet method with KBr, is shown in Fig. 5, together with the spectrum of the di-*n*-dodecyl phosphate used in this experiment. In the (a) spectrum in Fig. 5, a peak at about 1200 cm^{-1} disappears and a peak at about 1150 cm^{-1} appears. These peaks cannot be definitely assigned for the present, but the spectra show that dodecyl phosphate varies at the iron surface. From these infrared spectra, it can be thought that the iron atom is substituted for

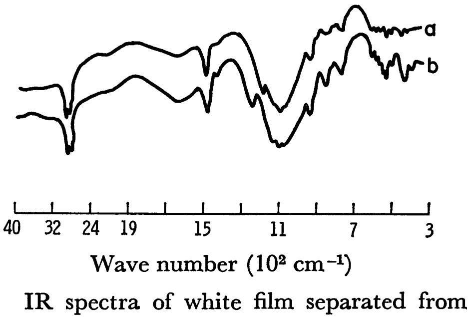

Fig. 5. IR spectra of white film separated from iron surface (a) and di-*n*-dodecyl phosphate (b).

one hydrogen atom in dodecyl phosphate at the iron surface.

TABLE 2. THE CONTENT OF Fe AND P IN THE SOLUTION DISSOLVED FROM WHITE FILM SEPARATED FROM THE IRON SURFACE[a]

Sample	Fe mg/cm^3	dodecyl phosphate mg/cm^3	Fe content in phosphate %
film A	0.025	0.575[b]	4.30[c]
film B	0.030	0.425[b]	6.98[c]
dodecyl phosphate	0.0013	1.50	0.08

a) Film separated from iron surface was dissolved in cyclohexane b) Content of dodecyl phosphate was calculated from the PK_α intensity. c) Weight of film separated from iron surface was calculated from content of dodecyl phosphate, supposing that film consisted of dodecyl phosphate.

Determination of Fe and P. The contents of Fe and P in the films separated from the iron surface are shown in Table 2. The content of the Fe impurity in the dodecyl phosphate used in this experiment is 0.08%. The content of Fe in the white film separated from the iron surface is between 4.3 and 6.9%. The composition in the films was not constant, but the Fe content in the films showed values in the range from about 4.3 to 6.9% in several experiments. The calculated value of the Fe content in the film is 4.3%, supposing that two molecules of dodecyl phosphate combine with the iron atom as Fe^{2-}, while the value is 6.4%, if we suppose that three molecules of dodecyl phosphate combine with the iron atm as Fe^{3-}. From these results, it was inferred that di-*n*-dodecyl phosphate reacted with the iron atom at the iron surface in the C_6H_{12} solution, that the iron atom was substituted for two or three molecules of dodecyl phosphate, and that the main component of the film formed on the iron surface was $[(RO)_2POO]_2Fe$ or $[(RO)_2POO]_3Fe$.

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