The Mechanism of Inhibition of the Corrosion of Iron by Solutions of Sodium Phosphate, Borate, and Carbonate.

By J. E. O. MAYNE and J. W. MENTER.

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The film formed on iron by 0·1N-solutions of disodium hydrogen phosphate, trisodium phosphate, sodium borate, and sodium carbonate, in the presence of air but in the absence of the air-formed film, has been removed by the alcoholic iodine method, and its composition determined by electron diffraction. All the films consisted mainly of a cubic oxide having the composition of Fe_3O_4, γ-Fe_2O_3, or an intermediate compound. When disodium hydrogen phosphate was used, large particles of $FePO_4,2H_2O$ were detected, embedded in a matrix of cubic oxide; trisodium phosphate yielded films containing only a small amount of ferric phosphate; with sodium carbonate and sodium borate no evidence was obtained for the existence of a second phase. The results are interpreted in terms of the hydrolysis and oxidation of the anodic product.

IN the preceding paper a mechanism was suggested for the inhibition of the corrosion of iron by solutions of sodium hydroxide; this paper is an account of an extension of that investigation to solutions of trisodium phosphate, disodium hydrogen phosphate, sodium borate, and sodium carbonate.

EXPERIMENTAL

Materials.—The iron used had the same composition as that used by Mayne and Pryor (*J.*, **1949**, 1831); the method of preparing the specimens was also identical.

In a preliminary investigation, freshly abraded specimens of iron, about 1 cm.^{2}, were totally immersed in 0·1N-solutions of the four inhibitors, contained in 100-ml. beakers; it was found that no corrosion occurred after 4 weeks' immersion, consequently 0·1N-solutions were used throughout this investigation.

Passivation of the Specimens.—Iron specimens, 5 × 1 cm., were passivated for 2 days in the four inhibitive solutions, containing dissolved oxygen, by the method previously described (Mayne and Pryor, *loc. cit.*), in which the air-formed film was first destroyed by treatment with dilute hydrochloric acid, which was then displaced by a large volume of the inhibitive solution. The film on the passivated specimens was stripped by Nurse and Wormwell's method (*J. Appl. Chem.*, 1952, **2**, 550), after which portions of the film were floated on to copper grids and examined by electron diffraction, the transmission method being used. This was carried out in a Metropolitan Vickers EM3 electron microscope.

Electron-diffraction Examination of the Stripped Films.—With the above electron microscope, it is possible to carry out a microscopic examination of the stripped film in transmission, and also to obtain a diffraction pattern from a selected area of the film either 10 μ or 2 μ in diameter, as described by Mayne, Menter, and Pryor (*J.*, **1950**, 3229). Electron-microscopic examination by this method showed that in all cases the stripped film had large continuous homogeneous areas of even thickness, but that in some regions there were denser particles, of the order of 1 μ or less in size.

Disodium Hydrogen Phosphate.—The homogeneous parts of the film gave patterns of slightly diffuse continuous rings corresponding to the Fe_3O_4 or γ-Fe_2O_3 cubic structure. However, in areas where there were denser particles the diffraction pattern was different. For example, in Fig. 1 is shown the pattern obtained from a region containing many particles rather less than

1 μ in size. The rings are discontinuous and consist of a large number of arcs and spots. Fig. 3 is the diffraction pattern from the area shown in Fig. 2, which contains an exceptionally large particle. The spotty rings are replaced by regularly arranged arcs indicating some preferred orientation in the growth of the particle. This is confirmed by the striations visible on the particle in the direction indicated by the arrow. The measured spacings obtained from these two photographs are listed in cols. 2 and 3 of Table 1. As before, the calibration of the pattern

TABLE 1.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Spacing (Å) of film formed in :			Fe_2O_3 *	$Fe_3(PO_4)_2$: †		$FePO_4,2H_2O$: †	
Na_3PO_4	Na_2HPO_4	Na_2HPO_4	Spacing, Å	Spacing, Å	Intensity	Spacing, Å	Intensity
—	—	8·82	—	—	—	8·72	—
—	—	—	—	7·94	0·5	—	—
—	—	6·88	—	6·73	1·0	—	—
6·11	—	6·15	—	—	—	6·1	0·4
—	5·58	—	—	—	—	5·5	0·8
4·78	4·83	4·93	4·82	4·87	0·5	4·9	0·6
—	—	4·68	—	4·54	0·4	—	—
—	4·34	4·36	—	4·36	0·05	4·36	1·0
—	4·17	—	4·16	—	—	—	—
3·92	3·93	—	—	4·02	0·03	4·00	0·6
—	—	—	—	3·83	0·75	—	—
3·65	3·65	3·67	—	3·66	0·05	3·70	0·5
3·45	3·43	3·46	—	—	—	3·43	0·4
—	3·29	3·32	—	—	—	3·29	0·5
3·15	3·19	—	—	3·195	0·60	3·12	0·8
3·02	2·98	2·99	—	2·98	0·60	2·99	0·7
2·93	—	2·93	2·935	—	—	—	—
2·88	2·83	2·84	—	—	—	2·86	0·7
2·78	—	—	—	—	—	2·79	0·2
—	2·74	—	—	2·725	0·50	—	—
2·68	2·71	2·68	—	—	—	2·69	0·2
2·59	2·65	—	2·63	2·634	0·08	2·62	0·2
2·53	2·53	2·53	—	—	—	2·54	0·8
2·50	—	—	2·51	2·515	0·20	—	—
2·41	2·43	—	2·41	2·414	0·25	2·43	0·6
2·36	2·33	—	—	—	—	2·36	0·4
2·29	2·27	2·31	—	2·315	0·05	2·28	0·2
—	—	—	—	2·233	0·05	—	—
2·19	2·19	2·18	2·18	2·183	0·03	—	—
2·16	2·14	2·14	—	—	—	2·13	0·6
2·09	2·08	2·08	2·08	—	—	2·09	0·2
2·06	2·03	—	—	2·066	0·05	2·06	0·5
2·00	2·00	—	—	—	—	2·00	0·6
1·94	1·95	—	—	1·955	0·03	1·96	0·6
1·91	1·92	1·88	1·91	1·919	0·40	1·90	0·4
1·83	1·86	—	1·86	1·82	0·02	1·83	0·4
—	—	—	—	—	—	1·80	0·5
—	1·78	1·75	—	1·772	0·03	1·76	0·5
1·73	1·74	1·71	—	—	—	1·72	0·4
1·71	1·72	—	1·70	—	—	—	—
1·69	1·69	—	—	—	—	1·69	0·4
1·66	—	1·66	—	1·667	0·60	1·65	0·6
—	1·64	—	—	1·632	0·03	1·63	0·7
—	1·63	—	—	—	—	—	—
—	1·60	—	1·60	—	—	1·61	0·7
—	1·59	—	—	1·587	0·40	1·598	0·7
—	1·57	—	—	—	—	1·569	0·6
1·54	1·56	—	—	1·55	0·04	1·555	0·6
1·53	1·54	—	—	—	—	1·54	0·4
—	1·47	1·47	1·47	1·461	0·05	1·479	0·7
—	1·43	1·445	—	—	—	1·44	0·6
—	—	—	—	1·422	0·06	1·42	0·4
—	1·415	—	1·415	—	—	1·411	0·4
1·40	1·405	1·40	—	—	—	—	—
—	1·37	—	1·375	—	—	—	—
—	1·325	1·295	1·31	—	—	—	—
—	—	1·24	1·245	—	—	—	—
—	—	1·21	1·195	—	—	—	

* Calculated from $a_0 = 8{\cdot}32$.

† A.S.T.M. Index.

Fig. 1.

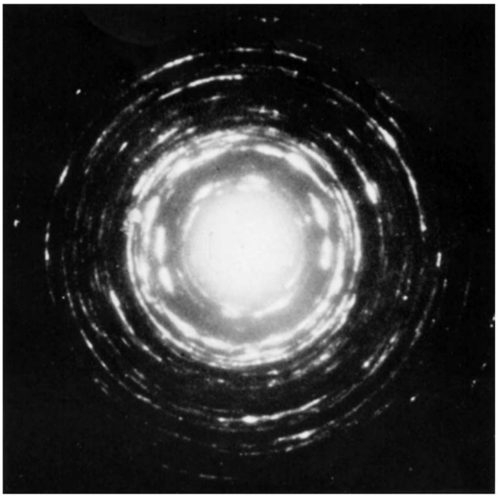
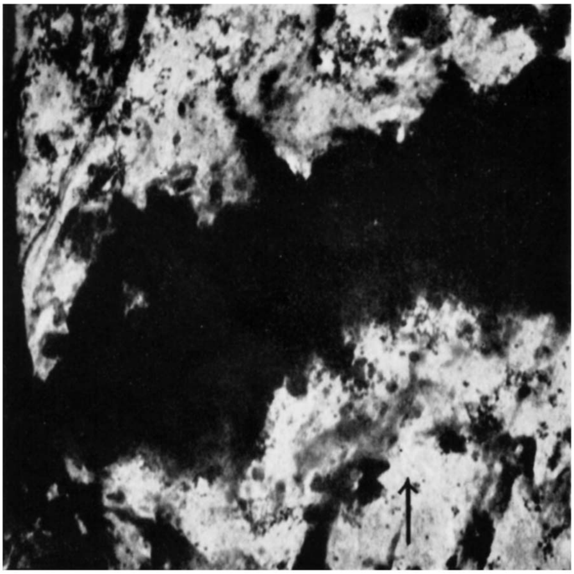


Fig. 2.



× 10,000.

[*To face p.* 104.

FIG. 3.

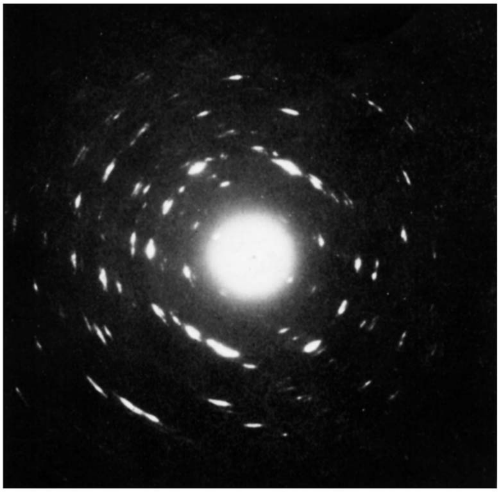
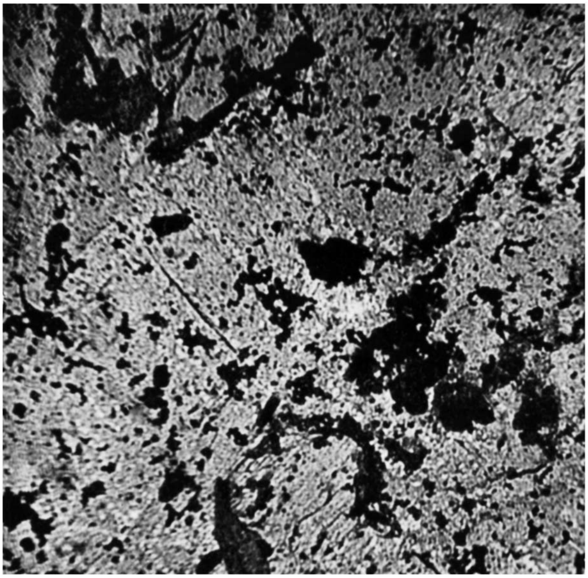
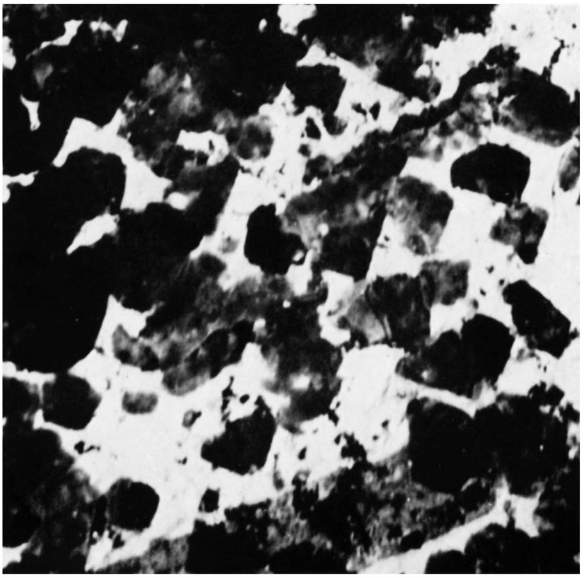


FIG. 4.



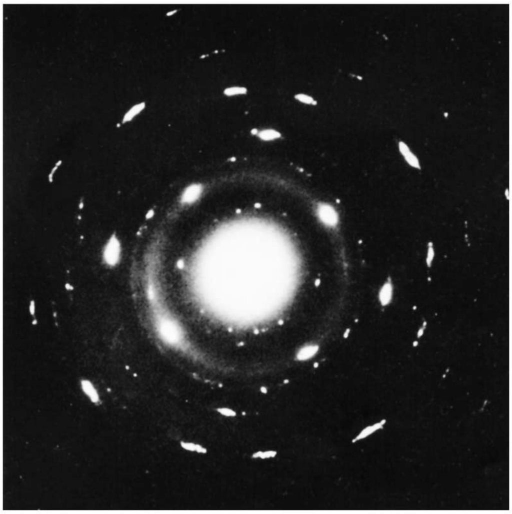
× 10,000.

Fig. 5.



× 10,000.

Fig. 6.



was made by selecting the 2·51-Å ring of the γ-Fe_2O_3 pattern as standard for the calculation of an equivalent λL for the pattern. The majority of determined spacings agree well with the *X*-ray values for strengite, hydrated ferric phosphate ($FePO_4,2H_2O$), col. 7. A few correspond to the cubic γ-Fe_2O_3, and arise from the film of which the particles form part, and a few may possibly be attributed to ferrous phosphate, the *X*-ray spacings of which are given in col. 5. The main constituent of these regions examined was undoubtedly hydrated ferric phosphate. It should be emphasized, however, that these patterns were obtained from very small areas of the film showing a high proportion of phosphate to oxide, deliberately chosen to enhance the pattern of the former for purposes of measurement. No deductions could be made from electron-diffraction evidence concerning the relative proportions of oxide to phosphate in the film.

Trisodium Phosphate.—As with disodium hydrogen phosphate, the films formed in trisodium phosphate solutions were found to consist of a basic continuous film of Fe_3O_4 or γ-Fe_2O_3, with particles of ferric phosphate either attached to or occluded in the film. In this case, however, the relative amount of ferric phosphate was very much smaller, so that the diffraction pattern consisted of Fe_3O_4 or γ-Fe_2O_3 continuous rings together with many individual diffraction spots corresponding to ferric phosphate. Values of spacings determined from a typical plate are given in col. 1 of Table 1. A typical area of the film is shown in Fig. 4.

Sodium Carbonate and Sodium Borate.—With both of these inhibitors the film consisted of Fe_3O_4 or γ-Fe_2O_3. In six photographs of different regions of a film stripped from a specimen immersed in sodium carbonate solution 18 rings were observed agreeing, within 0·5%, with the calculated values for γ-Fe_2O_3 as given in col. 4 of Table 1.

Some particles were observed in some of the films, but the diffraction spots from these generally coincided with the continuous rings from the γ-Fe_2O_3 film. An interesting example of such a specimen is shown in Figs. 5 and 6. The micrograph reveals a number of particles with cubic or rectangular outlines aligned nearly parallel to a preferred direction. The corresponding diffraction pattern shows a large number of cubic cross grating patterns, which are almost coincident. These larger particles of γ-Fe_2O_3 may have formed either during the build up of the inhibitive film, or by subsequent oxidation of particles of iron detached with the film during the stripping process. The former hypothesis seems more likely in view of the regular contours of the particles.

A few of the photographs showed weak diffraction spots not lying on the γ-Fe_2O_3 rings. The number of these was insufficient to determine unambiguously to what compound they should be attributed. They might easily arise from small quantities of impurity in the film, and their very small number indicates that they are probably not an essential constituent of the film.

Chemical Examination of the Stripped Film.—The presence of combined phosphate, in the films produced by both the dibasic and the tribasic salt, was confirmed by chemical analysis. The film was stripped from specimens of known area, no " Formvar " was used, and the stripped film, after being washed several times with methyl alcohol, was dissolved in three drops of concentrated hydrochloric acid, and the phosphate determined by the molybdenum-blue method, as described by Sandell (" Colorimetric Determination of Traces of Metals," Interscience Pub. Inc., New York, 1944, p. 137) for the determination of arsenic, hydrazine sulphate being used as the reducing agent and a Spekker photoelectric absorptiometer for determination of the intensity of the blue colour. The film produced by immersion in disodium hydrogen phosphate solution for 1 day contained 8·4 μg. of PO_4/cm.^{2}, and this value remained unchanged after a further 5 days. Another specimen immersed for 194 days yielded a film containing 4·0 μg. of PO_4/cm.^{2}. Trisodium phosphate produced, after 2 days, a film containing 0·4 μg. of PO_4/cm.^{2}, and after a further 3 days 0·2 μg. of PO_4/cm.^{2} was detected. Another specimen immersed for 51 days yielded a film containing 0·5 μg. of PO_4/cm.^{2}. The specimens treated with disodium hydrogen phosphate showed interference tints, whereas when trisodium phosphate was used the passivated specimens appeared unchanged.

The iron content of the films stripped from another set of specimens was also determined by means of thioglycollic acid. Very variable results were obtained. This was attributed to the presence of particles of metallic iron in the film, an explanation confirmed by the observation that on storage in methyl alcohol several fragments of film developed circular spots of rust.

Partial-immersion Tests.—In order to obtain further information regarding the mechanism of inhibition by solutions of dibasic and tribasic sodium phosphate, partial-immersion tests have been carried out with 0·1N-solutions, both of which were N with respect to sodium tartrate, added to dissolve ferric phosphate.

Mild-steel specimens, 3″ × 1″, the composition of which is given in the preceding paper, were used in two surface conditions : (1) freshly pickled in dilute hydrochloric acid; (2) pickled, in a similar manner, and stored in a desiccator over calcium chloride for one week. The specimens were weighed and partially immersed in the solutions contained in 60-ml. tall-form beakers, which were stored under a bell-jar in the laboratory. At the end of the experiment the specimens were scrubbed under the tap, dried, and reweighed; the losses in weight are shown in Table 2. Each experiment was performed in duplicate. It can be seen that when the surface of the specimens was freshly pickled the solution of disodium phosphate, which was N with respect to sodium tartrate, was corrosive; with this solution the attack was visible within one day. In all the other cases the solutions were inhibitive.

TABLE 2. *Partial-immersion tests.*

(All the solutions were N with respect to sodium tartrate.)

Solution	Change in wt. (g.)	Duration (days)	Solution	Change in wt. (g.)	Duration (days)
A. Air-formed film 1 *week old.*			*B. Freshly pickled specimens.*		
0·1N-Na_3PO_4	−0·0004, −0·0002	34	0·1N-Na_3PO_4	−0·0002, −0·0002	93
0·1N-Na_2HPO_4	−0·0002, −0·0001	34	0·1N-Na_2HPO_4	−0·2791, −0·1334	93

DISCUSSION

The composition of the films formed on iron by four inhibitive 0·1N-solutions, in the presence of air, has been determined by electron diffraction and, where phosphate was present, by chemical analysis. It should be noted that the films were formed on iron from which the air-formed film had been removed by acid treatment, and that film formation could occur in two ways, *i.e.*, by the direct reaction with oxygen in solution or by reaction with the inhibitive ions, including OH. Unfortunately, the relative rates of these two reactions are not known. It is probable that the films formed, in these circumstances, are richer in material produced from the inhibitive ions than passive films formed on specimens which initially carried an air-formed film.

The most striking fact which emerges from these experiments is that in all cases the films were composed mainly of a cubic oxide having the structure of Fe_3O_4, γ-Fe_2O_3, or an intermediate compound. When disodium hydrogen phosphate was used, large particles of $FePO_4,2H_2O$ were detected imbedded in a matrix of this cubic oxide. In the case of the tribasic salt the film contained only a small amount of ferric phosphate, which gave rise to a number of isolated spots and not continuous rings in the diffraction photographs. [Since this investigation was completed Pryor, Cohen, and Brown (*J. Electrochem. Soc.*, 1952, **99**, 542), working with radioactive phosphorus, have obtained somewhat similar results.] With sodium carbonate and sodium borate no clear evidence for the existence of a second phase was obtained.

Sodium carbonate, sodium borate, and trisodium phosphate are the salts of weak acids, and their aqueous solutions are alkaline owing to hydrolysis (the 0·1N-solutions had pH values of 11·2, 9·2, and 9·8, respectively); consequently, the ferrous compounds formed at the anodes will readily hydrolyse to ferrous hydroxide, which in alkaline solution oxidizes to an oxide having the cubic structure (*J.*, 1953, 129). On the other hand, 0·1N-disodium hydrogen phosphate has a pH of 8·4 and with this solution the ferrous phosphate formed at the anodes will be more stable to hydrolysis, but readily oxidized to ferric phosphate.

The question arises as to the relative inhibitive function of the oxides and phosphates in the film. With the dibasic salt, the partial-immersion tests (Table 2) indicate that when the air-formed film was thin the presence of phosphates in the film was necessary for inhibition; on the other hand, when the air-formed film was thick the presence of phosphates in the film was not necessary. With the tribasic salt only small quantities of phosphate were detected in the films, and the partial-immersion tests showed that these compounds were not essential for the development of passivity. It should be noted that in these immersion tests the solutions were N with respect to sodium tartrate, both ferrous and ferric phosphates being soluble in such a solution.

The conclusions to be drawn from this investigation are that when iron, carrying its air-formed film, is immersed in 0·1N-trisodium phosphate, -sodium carbonate, or -sodium borate in the presence of air, the weak areas in the air-formed film are repaired by the formation of γ-Fe_2O_3, Fe_3O_4, or an intermediate compound, as with 0·1N-sodium hydroxide. 0·1N-Disodium hydrogen phosphate behaves similarly, but forms some $FePO_4,2H_2O$, which may be essential for inhibition, particularly when the air-formed film is weak.

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DEPARTMENT OF METALLURGY, UNIVERSITY OF CAMBRIDGE.
LABORATORY FOR THE PHYSICS AND CHEMISTRY OF SURFACES,
DEPARTMENT OF PHYSICAL CHEMISTRY,
UNIVERSITY OF CAMBRIDGE.

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