392. *The Mechanism of Inhibition of Corrosion of Iron by Chromic Acid and Potassium Chromate.*

By J. E. O. Mayne and M. J. Pryor.

An examination has been made of the mechanism by which the corrosion of iron is inhibited by aërated solutions of chromic acid and potassium chromate. The view is put forward that the iron ions are oxidised, while still in the solid lattice, to γ-ferric oxide, which forms a thin continuous film on the iron. This film is impervious to iron ions, and thus corrosion is prevented.

The work described in this paper was designed to elucidate the mechanism by which aërated solutions of chromic acid and potassium chromate inhibit the corrosion of iron. Previous theories relating to inhibition by solutions of potassium chromate can be divided into three classes :

(1) The precipitation theory. Hoar and Evans (*J.*, 1932, 2476) examined the protective mechanism of potassium chromate solutions and concluded that inhibition was due to the plugging of weak points in the primary air-formed film by a mixture of hydrated ferric and chromic oxides (cf. Evans, " Corrosion Handbook," p. 9, 1948, John Wiley & Sons).

(2) The adsorption theory. Uhlig (*Chem. Eng. News*, 1946, 3154) put forward the view that inhibition by solutions of chromates was brought about by the adsorption of a unimolecular layer of chromate ions, in such a manner that they satisfied the secondary valency forces of the iron ions without disrupting the metal lattice.

(3) The oxide-film theory. Evans (*J.*, 1927, 1020; *Trans. Amer. Inst. Min. Met. Eng.*, 1929, 7) isolated the film from a freshly abraded iron specimen, which had been immersed in potassium chromate solution. He stated that " the main function of the chromate, in the case of electrolytic iron, is clearly to repair the discontinuities in the oxide film, which had already commenced to grow during the grinding in the air, but, in addition, there is some evidence that the chromate causes thickening of the film." Furthermore he showed that the film was not appreciably attacked by 0·1N-hydrochloric acid and concluded that it consisted of anhydrous ferric oxide as distinct from the hydrated product. His conclusion was supported by the electron-diffraction studies of Iitaka, Miyake, and Iimori (*Nature*, 1937, **39**, 156), which showed that the stripped film was composed of either γ-Fe_2O_3 or Fe_3O_4.

Both Evans and Iitaka *et al.*, however, passivated iron surfaces carrying a film of air-formed oxide, which has been shown to consist of γ-Fe_2O_3 (Iitaka, Miyake, and Iimori, *loc. cit.*; Nelson, *J. Chem. Physics*, 1937, **5**, 252; Vernon, *Trans. Faraday Soc.*, 1935, **31**, 1677). The films stripped from such passive specimens would consist of a mixture of the original air-formed oxide with any film produced by the chromate, and so it is not easy, from these experiments, to determine the exact function of the chromate. In the present work the action of chromates on oxide-free surfaces was investigated, to obtain further information on the part played by chromic acid and potassium chromate solutions during inhibition.

Experimental.

Materials.—The iron used in the film-stripping experiments was sheet 0·2 mm. thick. It was kindly supplied by the British Iron and Steel Research Association and had the following analysis : C, 0·005; Si, 0·0075; S, 0·013; P, 0·003; Mn, 0·007; Ni, 0·018; Cr, 0·02; Cu, 0·003; O, 0·12; N, 0·008; H, 0·00009%. Each specimen, measuring 4 × 1·5 cm., was degreased with xylene, abraded with 3/0 emery, swabbed with acetone, and dried, immediately before each experiment. In some experiments, discs 2 cm. in diameter and 1 mm. thick were required. These were cut from iron sheet of the same composition. The faces for examination were abraded, under alcohol, down to 4/0 emery and finally polished with magnesia on selvyt cloth, except when otherwise stated. The surfaces were then most carefully degreased in redistilled benzene and finally ethyl alcohol.

Pure chromic acid and AnalaR potassium chromate were used.

Passivation of the Specimens.—The specimens were immersed in 60 ml. of 0·2N-hydrochloric acid for 15 seconds, in order to remove the air-formed oxide film; the acid was then rapidly displaced upward by a large volume (1 l.) of the passivating solution. The operation was carried out in a glass tube, the bottom of which had been drawn down and sealed to a glass tap. A small side tube was sealed in near the top of the vessel to allow the excess of solution to run to waste. A large reservoir containing the chromate was connected to the bottom of this vessel by a rubber tube. The rate of flow of the chromate could be adjusted by altering the relative heights of the tube and reservoir. After the acid had been completely displaced, the tap at the bottom of the tube was closed and the specimen left in contact with the solution for the required period. During displacement of the hydrochloric acid by potassium chromate some chromic acid will be formed; the chromic acid will, however, be in contact with the metal only for a very short time and, since film formation is not instantaneous, this effect has been neglected. After this treatment the specimen was removed from the solution, washed rapidly in distilled water, and dried on filter paper.

Electron-diffraction Examination by the Reflection Method.—Specimens in the form of discs were passivated in M-chromic acid for 2 days and 0·1M-potassium chromate for six days by the method previously described. Further specimens, which had not been passivated, were immersed in 0·1N-hydrochloric acid for 10 seconds, washed carefully in distilled water, degreased in redistilled benzene, and allowed to grow air-formed oxide films for different times in a desiccator. The nature of the surface of these specimens was then examined by electron-diffraction, using the reflection method.

The type of pattern obtained from specimens carrying an air-formed film depended, not only on the time of exposure to air, but also on the abrasive pretreatment of the surface, as pointed out by Jackson and Quarrell (2nd Rep. of Alloy Steels Research Committee, I.S.I., 1939, **24**, 65). A specimen that had been abraded down to 3/0 emery, etched for 10 seconds in 0·1N-hydrochloric acid and exposed to dry air for 15 minutes, showed only an α-iron pattern when its surface was examined by reflection (Table I).

TABLE I.

Ring radius, R (cm.).	Spacing, *d* (A.).	Intensity.	*hkl.*	Lattice parameter, A.
0·73	2·05	S	110	2·90
1·02	1·43	M	200	2·86
1·28	1·15	S	211	2·82
1·62	0·905	M	310	2·86
1·94	0·755	M	321	2·83
2·15	0·68	W	330	2·88

Mean : 2·86 ± 0·04 A.

S = strong; M = moderate; W = weak.

TABLE II.

Ring radius, R (cm.).	Spacing, *d* (A.).	Intensity.	*hkl.*	Lattice parameter, A.
0·84	3·38	S	211	8·28
1·17	2·45	S	311	8·12
1·48	1·92	S	331	8·36
1·74	1·62	W	511, 333	8·41
1·94	1·47	S	440	8·31
2·14	1·22	S	444	8·44
2·67	1·04	W	800	8·32

Mean : 8·28 ± 0·16 A.

TABLE III.

Ring radius, R (cm.).	Spacing, *d* (A.).	Intensity.	*hkl.*	Lattice parameter, A.
0·87	4·2	W	200	8·4
1·49	2·5	S	311	8·29
2·35	1·5	S	440	8·46
3·02	1·2	W	444	8·30

Mean : 8·38 ± 0·08 A.

The lattice parameter was found to be 2·86 ± 0·04 A., gold-leaf being used for calibration; this is in good agreement with the *X*-ray value of 2·86 A. previously determined by Hull (*Phys. Review*, 1917, **10**, 661).

A specimen that had been abraded down to 4/0 emery, etched for 10 seconds in 0·1N-hydrochloric acid, and exposed to dry air for 30 minutes gave a more diffuse iron pattern, together with two broad oxide haloes, at spacings of approx. 2·5 and 1·5 A., when its surface was examined by reflection (cf. Nelson, *loc. cit.*). Exposure of a similarly treated specimen to dry air for 48 hours gave a series of sharp rings characteristic of either γ-Fe_2O_3 or Fe_3O_4. In this case no iron rings could be detected.

A specimen that had been passivated in M-chromic acid for 2 days, when examined by the reflection method, gave a ring pattern in reasonable accord with that of γ-Fe_2O_3 or magnetite. In this case the rings obtained were quite sharp, and there was no evidence of reflection from the underlying iron. The results are recorded in Table II.

The mean value of the lattice parameter was found, using gold-leaf for calibration, to be 8·28 ± 0·16 A.

The specimen that had been passivated for six days in 0·1M-potassium chromate solution gave a series of diffuse haloes when its surface was examined by reflection. As in the case of the specimen passivated in chromic acid, there was no evidence of reflection from the underlying iron. The calculated values of the spacings were in reasonable accord with either γ-Fe_2O_3 or Fe_3O_4. The results are shown in Table III.

The calculated value of the lattice parameter was found, using gold-leaf as calibration, to be 8·38 ± 0·08 A., in fair agreement with the values found in the previous experiments.

Isolation of the Film.—The films on the passivated specimens were stripped from the metal by the method of Vernon, Wormwell, and Nurse (*J.*, 1939, 621), except that the solutions were moved through the apparatus by means of a partial vacuum. Each specimen was treated with a solution of iodine in dry methyl alcohol, in an atmosphere of nitrogen; after 30—90 minutes, the solution was removed and the specimen washed with dry methyl alcohol. The specimen was then transferred to a dish of dry alcohol, and the film detached by gentle agitation.

Several of the larger pieces of film were floated on to fine copper gauzes and examined by electron diffraction. The remaining portions, which were feebly magnetic, were examined by chemical tests.

Chemical Examination of the Film Substance.—Portions of the film were suspended in M-chromic acid, and 0·1N- and 2N-hydrochloric acid. There was no evidence of attack, when the film was examined under the microscope, after 4 days' treatment with M-chromic acid or with 0·1N-hydrochloric acid, whereas samples of ferric and chromic hydroxide, both in the freshly precipitated and aged (1 week) condition, dissolved in a few minutes in either reagent. The hydroxides were prepared by shaking solutions of ferrous salts and potassium chromate, and those of ferric, ferrous, and chromium salts with sodium hydroxide or ammonium hydroxide. At a magnification of 500, attack on the film substance could just be detected after 24 hours' treatment with 2N-hydrochloric acid; samples of rust, however, prepared by partly immersing steel specimens in distilled water, tap water, or sea-water, were dissolved by this treatment.

A portion of the film, obtained by passivation in potassium chromate solution, was dissolved in 5N-hydrochloric acid; the solution was found to be free from ferrous ions when tested with di-2-pyridyl. The total iron was then determined colorimetrically with thioglycollic acid, and from these results and the known sensitivity of the di-2-dipyridyl test it was estimated that the film substance contained less than 2·5% of ferrous iron. Magnetite, when tested in a similar manner, gave a positive reaction with di-2-pyridyl, even after 2 hours' contact with an alcoholic solution of iodine.

Electron-diffraction Examination of Stripped Films by Transmission.—The film stripped from iron passivated for 2 days in M-chromic acid showed a well-defined ring structure characteristic of either γ-Fe_2O_3 or Fe_3O_4. The calculated values of the spacings are shown in Table IV.

TABLE IV.

Ring diameter, D (cm.).	Spacing, *d* (A.).	Intensity.	*hkl.*	Lattice parameter (A.).
1·58	4·18	W	200	8·36
2·26	2·92	M	220	8·26
2·63	2·51	VS	311	8·32
2·98	2·22	M	321	8·31
3·19	2·07	S	400	8·28
3·87	1·705	W	422	8·35
4·14	1·59	M	511, 333	8·27
4·52	1·46	S	440	8·26
5·28	1·25	W	622	8·29
6·35	1·04	W	800	8·32
7·92	0·835	VW	933	8·31
			Mean :	8·30 ± 0·06 A.

VS = very strong; VW = very weak; cf. also Table I.

The mean value of the lattice parameter was found, using gold-leaf as a standard, to be 8·30 ± 0·06 A., in good agreement with the previously determined value of 8·30 A. (Wyckoff, " Structure of Crystals," 1931, p. 267, American Catalog Co., Inc.) for γ-Fe_2O_3. Furthermore there was considerable evidence of a preferred orientation in the film. All the rings obtained were characteristic of the γ-Fe_2O_3 structure, and there was no evidence of the presence of a second phase. There was, however, a certain incoherent scattering of electrons which resulted in a lessening of contrast around the central spot.

The film stripped from iron passivated for two days in M-potassium chromate gave only diffuse oxide haloes when examined by transmission. A specimen was, therefore, passivated in 0·01M-potassium chromate solution for 14 days, and the film stripped from it. This film, when examined by transmission, gave an extremely good ring pattern characteristic of either γ-Fe_2O_3 or Fe_3O_4. The values of the spacings are shown in Table V.

TABLE V.

Ring diameter, D (cm.).	Spacing, *d* (A.).	Intensity.	*hkl.*	Lattice parameter (A.).
2·13	2·93	M	220	8·29
2·48	2·51	VS	311	8·32
2·99	2·085	S	400	8·34
3·24	1·92	W	331	8·36
3·64	1·71	W	422	8·36
3·89	1·60	M	511, 333	8·31
4·23	1·47	S	440	8·32
4·87	1·28	W	533	8·38
5·10	1·21	W	444	8·38
5·68	1·11	W	642	8·30
			Mean :	8·34 ± 0·04 A.

The mean value of the lattice parameter was found, using gold-leaf for calibration, to be 8·34 ± 0·04 A., which agrees well with that found in the previous experiment with chromic acid (8·30 ± 0·06). Incoherent scattering of the electrons was again observed, but there were no rings that indicated the presence of a second phase.

DISCUSSION.

An iron specimen, abraded down to 4/0 emery and exposed to dry air for 30 minutes, gave an α-iron pattern together with two diffuse oxide haloes. According to Miley and Evans (*J.*, **1937,** 1295), the mean thickness of the air-formed oxide film, after 30 minutes' air exposure, is 160 A. If, however, the oxide film was allowed to grow in air for 48 hours, after which time its thickness will be about 200 A. (Miley and Evans, *loc. cit.*), the pattern obtained by reflection was characteristic of either γ-Fe_2O_3 or magnetite. The film formed by passivation in either chromic acid or potassium chromate solution gave rings that fitted approximately with either the γ-Fe_2O_3 or the Fe_3O_4 structure. With the specimen passivated in chromic acid an anomalous reflection was observed from the (211) plane. This is a forbidden reflection for the face-centred cubic spinel type of structure, and is characteristic of a lower form of symmetry. This line has previously been observed by Iimori (*Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1937, **34**, 60), using *X*-rays, and also by Haul and Schoon (*Z. physikal. Chem.*, 1939, *B*, **44**, 216), and thus probably is a true function of the oxide structure and not merely due to the relaxing of the third Laue condition during electron diffraction, as pointed out by Jackson and Quarrell (*loc. cit.*). As no iron rings were observed, the film formed during passivation is clearly thicker, or more continuous, than the oxide film formed by 30 minutes' air exposure; it cannot, therefore, consist of a unimolecular layer of chromate ions, which is claimed by Uhlig to be responsible for passivity. Internal stresses in the film could arise from the fact, originally pointed out by Pilling and Bedworth (*J. Inst. Metals*, 1923, **29**, 529), that an increase in volume accompanies the conversion of iron into oxide. It is probable that it is these internal stresses which are directly responsible for the fact that the patterns obtained by reflection are characteristic of the distorted γ-Fe_2O_3 or Fe_3O_4 structure.

The stress relief that undoubtedly accompanies film stripping leads to the production of very good ring patterns by transmission, possibly by allowing recrystallization of the film substance. The film stripped from specimens passivated in chromic acid or dilute potassium chromate solution gave well-defined ring patterns which were in excellent accord with either the γ-Fe_2O_3 or the Fe_3O_4 structure. All the rings, except one, marked permissible reflections for either structure. It was clearly brought out, in the case of specimens passivated in chromic acid, that reflection from the (321) plane was occurring. This is an impossible reflection for the face-centred cubic spinel type of structure and is characteristic of a lower form of symmetry—probably either the primitive or body-centred cube. This reflection has previously been observed from γ-Fe_2O_3, by use of *X*-rays (Bannister, " Index of *X*-Ray Diffraction Constants," A.S.T.M., 1945, Haul and Schoon, *loc. cit.*), but never from magnetite. Goldschmidt (*J. Iron and Steel Inst.*, 1942, **146**, 157P) has pointed out the close crystallographic resemblance between α-iron, ferrous oxide, and magnetite, and has indicted how these two oxides can be built up from the α-iron lattice with a minimum of rearrangement of the iron atoms. Magnetite, which has the face-centred cubic spinel structure, contains 24 iron (16 ferric and 8 ferrous) and 32 oxygen atoms per unit cell. According to Verwey (*J. Chem. Physics*, 1935, **3**, 593), γ-Fe_2O_3 has a practically identical structure with 32 oxygen atoms and, on the average, only 21·3 iron (ferric) atoms in the unit cell. The γ-Fe_2O_3 lattice, therefore, contains more vacant sites than that of magnetite and might be expected, in some circumstances, to show evidence of a lower form of symmetry. There is, however, additional evidence to support the view that the film is largely composed of γ-Fe_2O_3 and not Fe_3O_4. The chemical examination of the film substance indicated that it contained less than 2·5% of ferrous ions. Furthermore, the stripped film was only feebly magnetic. These points, taken in conjunction with the electron-diffraction data, make it probable that the film formed during passivation in solutions of chromic acid or potassium chromate, is largely composed of γ-Fe_2O_3.

The transmission photographs of the stripped films all indicate the presence of a certain amount of incoherent scattering of the electron beam, which results in a decrease in contrast around the central spot. This may imply that a certain amount of the film substance is without characteristic interatomic distance, possibly owing to some residual internal stress. Furthermore, as some of the stripped films show a marked preferred orientation, probably inherited from the underlying metal, which was in the rolled condition, it is probable that the film is built as a continuation of the α-iron lattice, and not merely laid on the metal.

It is now considered by the authors that the objection, previously raised, that film stripping may alter the constitution of the surface layer (Jackson and Quarrell, *loc. cit.*), is no longer valid. It has been demonstrated that the stripped film gives patterns similar to those of the oxide in contact with the metal. The only effect of stripping is probably to allow recrystallisation of the film substance, which produces clearer patterns.

The observations, that the film substance is composed largely of γ-Fe_2O_3, which has been found to be visibly unattacked by 2N-hydrochloric acid, and that precipitated hydrated oxides, produced by a homogeneous reaction in solution, were very readily soluble in this reagent, indicate that chromate ions must have reacted with the iron ions before they had left the solid lattice; for had the iron ions passed into solution, they would have become hydrated and been precipitated as a hydrated product. Thus inhibition must be considered, not as a homogeneous reaction between two ions in solution, but rather as a heterogeneous reaction between ions in solution and the iron surface. Probably, the first step in the reaction is an adsorption of chromate ions on the iron surface, and this is followed by oxidation of the iron and reduction of the chromate ion. The chromate ion may be destroyed (i) by oxidising the iron directly, (ii) by reduction at cathodic areas on the metal, or (iii) by interaction with hydrogen atoms adsorbed on adjacent cathodic areas, as suggested by Pyke and Cohen (*J. Electrochem. Soc.*, 1948, **93**, 63). Whichever of these mechanisms is correct, the oxide film will thicken, either by migration of iron ions outward or by the crack-heal mechanism suggested by Evans (*Nature*, 1946, **157**, 732) (or both), until it becomes almost impermeable to iron ions. When this state is attained, the iron will have become passive, provided that sufficient inhibitor is present to heal any cracks subsequently produced in the film.

The electron-diffraction examination failed to indicate the presence of any phase except γ-Fe_2O_3. If any chromium compounds are present in the film, they will be there in amounts less than 10%. Clearly this is much less than the stoicheiometric proportion of tervalent chromium formed in the equation $2K_2CrO_4 + 5H_2O + 2Fe = Fe_2O_3 + 4KOH + 2Cr(OH)_3$.

In common with iron and aluminium hydroxide, the first amounts of chromic hydroxide would be expected to form colloidally, and so it is not surprising that tervalent chromium compounds appear in the film only in very small amounts, as shown by Hoar and Evans (*loc. cit.*). Films formed by passivation in M-chromic acid (pH 0·5) probably contain no chromic compounds, as the hydrated tervalent chromic ions would be readily soluble at this pH. In the case of potassium chromate, the chromic hydroxide, formed by the reduction of the chromate ion, may well interfere with the grain growth of the γ-Fe_2O_3 film. The film stripped from a specimen passivated for two days in M-potassium chromate solution gave diffuse rings characteristic of oxide with a very small crystal size. Passivation in 0·01M-potassium chromate for a much longer time (14 days), in which case the film would be expected to grow much more slowly and have a larger grain size, produced a film that gave very clear oxide pattern by transmission.

It should be noted that throughout this investigation no attempt has been made to separate the effect of oxygen in solution from that of the chromate ion. Darrin (*Ind. Eng. Chem.*, 1945, **37**, 741) has shown, however, that chromates can inhibit in the absence of oxygen.

The authors are indebted to the British Iron and Steel Research Association, and the Department of Scientific and Industrial Research, for financial assistance and to Dr. U. R. Evans, in whose laboratory the work was carried out, for encouragement and advice. They also acknowledge the helpful co-operation of Dr. V. E. Cosslett, Mr. J. W. Menter, and Mr. J. V. Sanders, in carrying out the electron-diffraction examination, and of Dr. F. Wormwell, Miss D. M. Brasher, Dr. N. F. M. Henry, Dr. T. P. Hoar, Dr. J. N. Agar, and Dr. M. Cohen for useful criticism.

METALLURGICAL LABORATORY, UNIVERSITY OF CAMBRIDGE. [*Received, February* 15*th*, 1949.]