The Mechanism of Inhibition of the Corrosion of Iron by Sodium Hydroxide Solution. Part II.*

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The film formed on iron by the anodic discharge of hydroxyl ions is composed of material having the cubic structure of either Fe_3O_4 or γ-Fe_2O_3; consequently it is indistinguishable from the air-formed film. Freshly abraded iron becomes passive when immersed in 0·1N-sodium hydroxide containing dissolved oxygen. It is suggested that weak areas in the air-formed film are first repaired by the electrochemical formation of ferrous hydroxide, which then reacts with oxygen to form material having the cubic structure of Fe_3O_4, γ-Fe_2O_3, or an intermediate compound; later repair may occur by the direct electrochemical production of ferric oxide; in this way the film thickens until it becomes impervious to ions and passivity ensues.

THE inhibition of the corrosion of iron by solutions of sodium hydroxide was discussed in Part I,* in which it was shown that when iron, freed from its air-formed film, was immersed in 0·1N-sodium hydroxide containing dissolved oxygen, it became covered with a film composed mainly of material having the cubic structure of either Fe_3O_4 or γ-Fe_2O_3, together with traces of γ-Fe_2O_3,H_2O. It was suggested that the material having the cubic structure arose from a reaction between oxygen and the surface iron atoms in a manner similar to that which gives rise to the air-formed film, whilst the γ-Fe_2O_3,H_2O was formed by the oxidation of ferrous hydroxide produced by the anodic discharge of hydroxyl ions on the metal surface. This view, regarding the origin of the hydrated oxide, was in accordance with the work of Kabanov and his co-workers (Kabanov, Burstein, and Frumkin, *Discuss. Faraday Soc.*, 1947, **1**, 259; Kabanov and Leikis, *Acta Physicochem. U.R.S.S.*, 1946, **21**, 769), who concluded that when iron, previously reduced in hydrogen, was anodically polarised in 2N-sodium hydroxide it became covered with a film of hydrated ferric oxide.

In the following investigation the anodic polarisation of iron in 0·1N-sodium hydroxide, in the presence and in the absence of air, has been examined; in general, the Russian results have been confirmed, but the oxide film has been found to be anhydrous and similar to the air-formed film. The results suggested that in the inhibition of the corrosion of iron by sodium hydroxide the function of oxygen is to oxidise the ferrous hydroxide, formed by an electrochemical mechanism, to a ferric compound having a structure indistinguishable from the air-formed film.

EXPERIMENTAL

Materials.—Two types of iron were used in this investigation. The first was Swedish iron containing a relatively large quantity of oxygen in the form of magnetite and it was used in the electron-diffraction experiments; its composition has been reported by Mayne and Pryor (*J.*, 1949, 1831). The second was annealed mild steel, in the form of sheet 0·014″ thick, which was used mainly in the polarisation experiments; it had the composition: C, 0·06; S, 0·021; P, 0·015; Mn, 0·36; Ni, 0·048; Cu, 0·040; Sn, 0·008%; Si, trace only.

Unless otherwise stated all the specimens were degreased in benzene, abraded with 3/0 emery, washed in benzene followed by acetone, and dried on filter-paper immediately before use.

Effect of Anodic Polarisation in the Presence of Air on the Composition of the Film.—Iron specimens, 3×1 cm., were immersed to a depth of about 1 cm. in 0.1N-sodium hydroxide and anodically polarised at constant current density; the cathode of the cell was a platinum wire immersed in the solution, but remote from the anode. In order to polarise the anode at constant current density, the cell, connected in series with a microammeter and a resistance, was inserted into the normal potentiometer circuit; thus by varying the position of the moving contact the potential across the cell could be adjusted and a constant current maintained. This method was used in all polarisation experiments throughout this investigation.

Freshly abraded specimens were polarised at 12.5 and $50\mu A/cm.^2$, and the polarisation was continued until the potential across the cell became constant owing to the evolution of oxygen. In some experiments the specimens were connected to the potentiometer before immersion, so that there was no time lag between contact with the solution and the flow of current; in others,
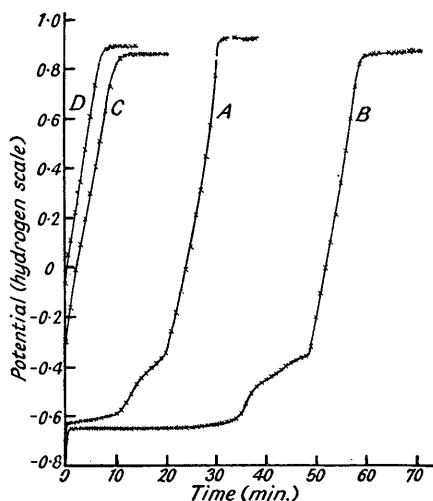
The anodic polarisation of iron in 0.1N-sodium hydroxide.

Curve *A*. Iron in the absence of air and the air-formed film. 19.4 Microamp./cm.².
Curve *B*. Steel in the absence of air and the air-formed film. 21.2 Microamp./cm.².
Curve *C*. Freshly abraded steel in the absence of air. 15.0 Microamp./cm.².
Curve *D*. Freshly abraded steel in the presence of air. 14.7 Microamp./cm.².

the air-formed film was removed by treatment with dilute hydrochloric acid before immersion in alkali.

The film was then removed from the passive specimens by the alcoholic iodine method of Vernon, Wormwell, and Nurse (*J.*, 1939, 621); portions of the stripped film were next floated on to copper grids and examined by electron diffraction, the transmission method being used.

In all cases the film appeared to be composed of material having the cubic structure of Fe_3O_4 or γ-Fe_2O_3. No conclusive evidence for the presence of γ-Fe_2O_3,H_2O was obtained but numerous spots which could be attributed to lepidocrocite were observed. Thus the film had the same composition as that removed from iron after treatment with 0.1N-sodium hydroxide in the presence of air, and the anodic treatment did not increase the amount of γ-Fe_2O_3,H_2O in the film.

Anodic Polarisation of Iron and Steel in the Absence of Air.—In order to examine the anodic polarisation of iron, in the absence of air and the air-formed film, use was made of an apparatus described in Part I. The efficiency of the vacuum system was improved by the insertion of a mercury diffusion pump and a McLeod gauge between the apparatus and the Hyvac pump and by the use of a slower de-aeration cycle. The modified experimental procedure was as follows. The side tubes, containing 0.1N-sodium hydroxide and 0.001N-hydrochloric acid, were immersed in liquid air, and the apparatus was evacuated for 30 min.; the pump was then turned off and the frozen solutions were allowed to melt; when the apparatus had reached room temperature the pump was connected for about 30 sec. This cycle of operations was repeated four times.

The iron specimen, 2.7×1.2 cm., was suspended from a platinum hook by means of a thin, soft-iron wire which passed through a hole in the specimen. The air-formed film was first removed by treatment with the hydrochloric acid, which was subsequently drained off and replaced by the 0.1N-sodium hydroxide. The small quantity of hydrochloric acid remaining on

the specimen and on the walls of the apparatus allowed the Ag–AgCl electrode to function; the potential of the iron specimen could consequently be measured, and at the end of the experiment the concentration of chloride ions in the solution was determined by means of another Ag–AgCl electrode. The potentials were measured by means of a Cambridge valve potentiometer. After the solution had been in contact with the specimen for about 30 min., the potential became constant and the specimen was anodically polarised at constant current density, the cathode being a platinum wire sealed through the wall of the apparatus.

The polarisation curve obtained at a current density of $19\cdot4\mu A/cm.^2$ is shown in curve *A* (in which the potentials are expressed on the hydrogen scale). At the end of the experiment the invisible film formed on the specimen was removed and examined by electron diffraction; it had the same composition as that produced by anodic polarisation in the presence of oxygen.

The experiment was repeated with a mild steel specimen. This was covered with annealing scale; consequently, it was degreased in benzene, pickled in dilute sulphuric acid, abraded with 3/0 emery, washed with benzene followed by acetone, and etched in dilute sulphuric acid for 5 sec. before being dried on filter-paper and placed in the apparatus—a treatment similar to that used by Kabanov and Leikis (*loc. cit.*). The air-formed film was removed by treatment with $0\cdot01$N-hydrochloric acid. The anodic polarisation curve obtained is shown in curve *B*. The film on the specimen was straw-coloured at the end of the experiment.

In another experiment the anodic polarisation was examined of a mild-steel specimen carrying its air-formed film. The procedure was similar to that used in the previous measurement except that the specimen, which was freshly abraded, was not treated with hydrochloric acid in the vacuum-apparatus; the side arm, which normally contained acid, was sealed off, and after de-aeration the alkali was transferred to the polarisation cell; in these circumstances the solution was rendered $0\cdot0001$N with respect to chloride ions in order to permit the Ag–AgCl electrode to function. The results obtained are shown in curve *C*.

Anodic Polarisation of Steel in the Presence of Air.—Mild-steel specimens, 3×1 cm., were freshly abraded and masked with hot paraffin wax so that an area $0\cdot75$—$1\cdot50$ cm.^{2} remained uncovered at one end; at the other end a small area was left uncoated in order to make electrical connection. The specimens were then partially immersed in $0\cdot1$N-sodium hydroxide, rendered $0\cdot0001$N with respect to sodium chloride, contained in an open beaker, and anodically polarised at constant current density. The cathode was a platinum wire immersed in the solution but remote from the specimen; the potential of the steel specimen was measured against an Ag–AgCl electrode. The results obtained are shown in curve *D*.

DISCUSSION

In Part I the presence of lepidocrocite in the film was inferred from a number of spots obtained in electron-diffraction photographs; it was suggested that the γ-Fe_2O_3,H_2O arose from the oxidation of ferrous hydroxide produced by the anodic discharge of hydroxyl ions on the metal surface. If this hypothesis regarding the mode of formation of γ-Fe_2O_3,H_2O is correct, it ought to be possible to increase the concentration of lepidocrocite in the film, by anodic polarisation, to such an extent that rings would be produced in the electron-diffraction photographs. Efforts to carry this out have been unsuccessful, indicating that γ-Fe_2O_3,H_2O is not formed by anodic polarisation.

Kabanov *et al.* (*loc. cit.*) concluded, from a consideration of anodic polarisation curves, that iron reduced in hydrogen and polarised in 2N-sodium hydroxide became covered with a film of hydrated oxide. Their experiments have beeen repeated in $0\cdot1$N-solution under slightly different conditions, and the film has been examined by electron diffraction; it was found to consist mainly of a material having the cubic structure of either Fe_3O_4 or γ-Fe_2O_3.

When iron or steel initially freed from air-formed films is used, the anodic polarisation curves obtained in the absence of oxygen are similar to those obtained by Kabanov *et al.* in that they all show three arrests, indicating that at least three different processes are taking place on the metal surface. This confirmation is very satisfactory, particularly in view of the fact that (1) the authors removed air-formed films with acid and not hydrogen, (2) measurements were made in a vacuum-apparatus and not in an atmosphere of hydrogen.

The first arrest has been attributed by Forster (*Z. Elektrochem.*, 1910, **16**, 461) and Kabanov and Leikis (*loc. cit.*) to the formation of a film of ferrous hydroxide on the surface

of the iron; this conclusion appears reasonable, although the process occurs in $0 \cdot 1$N-sodium hydroxide at about $-0 \cdot 63$ v, which is a more positive value than that calculated from the equilibrium potential of the system Fe–Fe(OH)$_2$. Kabanov and Leikis have discussed this point at some length and have put forward the view that the formation of ferrous hydroxide is brought about by the hydrolysis of an anion such as HFeO$_2'$.

The second arrest, which is generally half the length of the first, is considered to be due to the oxidation of ferrous hydroxide to ferric compounds, which have been found to be composed mainly of anhydrous oxide having the structure of Fe$_3$O$_4$ or γ-Fe$_2$O$_3$. In $0 \cdot 1$N-sodium hydroxide this arrest appeared to consist of two parts, which suggests that the oxidation proceeds *via* the intermediate formation of magnetite. In this connection it should be noted that recent work by one of the authors (Mayne, *J.*, 1953, 129) has shown that in alkaline solutions, with a slow rate of oxidation, ferrous hydroxide is converted into a product having a composition intermediate between Fe$_3$O$_4$ and γ-Fe$_2$O$_3$.

The third arrest corresponds to the liberation of oxygen, the specimen having become passive. It has been found that in the absence of air and the air-formed film the iron requires 36 millicoulombs/cm.^{2} and the steel 76 millicoulombs/cm.^{2} for this to take place. The difference in value may be attributed to the fact that the iron, being purer, was more easily covered by a passive film, since film growth could proceed relatively undisturbed by inclusions; it should be noted that the air-formed film was removed by treatment with acid, which was more concentrated when steel was used so that the surface of the steel was rougher.

Both the first and the second arrest were absent from the polarisation curves obtained with abraded specimens, which carried their air-formed films; Kabanov *et al. (loc. cit.)* obtained a similar effect with film-free specimens after they had been in contact with oxygen. In the presence of air the polarisation curve was shifted to the left, *i.e.*, the specimen became passive more readily, thus indicating that oxygen plays an important part in passivation.

In Part I *(loc. cit.)* it was shown that freshly-abraded iron became passive when immersed in $0 \cdot 1$N-sodium hydroxide, in the presence of air, and acquired a potential of about zero on the hydrogen scale. When a freshly abraded specimen was polarised, in the absence of oxygen, $2 \cdot 0$ millicoulombs/cm.^{2} were required to polarise the specimen to zero; this quantity of electricity corresponds to an increase in thickness of the oxide film of 10 Å. Vernon, Wormwell, and Nurse *(J.*, 1939, 621) estimated that the thickness of the air-formed film on freshly abraded iron was of the order of 140 Å; it is difficult to see how an additional 10 Å could render the iron passive, and it seems more probable that passivity is brought about by repair of weak areas in the air-formed film.

In the presence of air and in the absence of applied current the specimen acquired the potential of zero after about 30 minutes' immersion. In the polarisation experiment carried out in the presence of air this time was reduced to little more than 1 min.; consequently, the normal electrochemical process, which is responsible for film repair in the absence of applied current, can have played little part in the polarisation experiment. Thus an air-formed film, which may be months old, can be rapidly reinforced by immersion in $0 \cdot 1$N-sodium hydroxide, in the presence of air, with or without the application of a current. Three hypotheses can be advanced in order to explain this : (1) the air-formed film breaks down upon immersion in the solution; (2) oxygen in solution is more active than in the gaseous form; (3) oxygen reacts more readily with the anodic product than with the air-formed film. There appears to be little evidence in support of hypotheses (1) and (2); hypothesis (3), however, provides an explanation, since the anodic product in alkaline solution will be ferrous hydroxide. The main function of oxygen is to stimulate the cathodic reaction, but it may also oxidize ferrous hydroxide to Fe$_3$O$_4$, γ-Fe$_2$O$_3$, or an intermediate compound and, if all the repairing substance is produced by this mechanism, the quantity of current required to polarise the specimen to zero, in the presence of air, would be in the range $1 \cdot 3$—$1 \cdot 5$ millicoulombs/cm.^{2}. The value obtained was $1 \cdot 2$ millicoulombs/cm.^{2} (curve *D*); thus a small quantity of the repairing substance may be formed by a different mechanism. These results suggest that, when abraded steel is immersed in $0 \cdot 1$N-sodium hydroxide, weak areas in the air-formed film are reinforced by the electrochemical formation of ferrous hydroxide, which reacts with oxygen to form an oxide, probably having

a structure intermediate between Fe_3O_4 and γ-Fe_2O_3, and is thus indistinguishable, by electron diffraction, from the air-formed film. This reaction continues until a potential of about -0.4 v is reached, after which repair can take place by direct electrochemical formation of ferric oxide.

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