660. *The Passivity of Metals. Part XI.* The Anodic Behaviour of Iron Oxide Films.*

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A study has been made of the behaviour of iron, coated with visible oxide film by previous heating in air, when subjected to anodic treatment in dilute sulphuric acid. Measurements have been made of the time needed for the destruction of the oxide film by auto-reduction after interruption of the current; this break-down time (t_b) increases with increase of the time (t_c) during which the current flows before the interruption. The increase in t_b is attributed to the increase in the oxygen-charge built up by the anodic polarisation. The scatter of the results is probably due to intermittent cracking of the film. Similar results have been obtained at different current densities and at different temperatures, although auto-reduction occurs much more rapidly at 24° than at 6°.

Earlier work (Pryor and Evans, *J.*, 1950, 1259) has attributed the rapid destruction of the films on heat-tinted iron placed in dilute sulphuric or hydrochloric acid to the cell,

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* Part X, *J.*, 1949, 3330.

Fe (anode) | acid | Fe_2O_3 (cathode), set up at certain sensitive points; these may be either definite gaps in the film or places rich in lattice defects where iron cations from the metal can migrate outwards through the film substance. The reduction process by the local cells is termed auto-reduction. Powdered ferric oxide placed on mercury, covered with acid and joined by an external wire to an iron anode also dipping into the acid, suffers reductive dissolution in the same way as an oxide film clinging to its iron basis; ferric oxide passes into solution as ferrous ions (*idem, ibid.*, p. 1266). The direct attack on the ferric oxide powder (in absence of cathodic polarisation) is much slower (*idem, J.*, 1949, 3330); likewise, ferric oxide films, after separation from the metallic basis, can be kept in acid for long periods without dissolution. Heat-tinted iron, which, when placed in dilute sulphuric acid, loses its colour within a few seconds, retains the colour unchanged for 24 hours if chromic acid also is present in sufficient amount (Evans, *J.*, 1930, 481). In the presence of chromic acid, a powerful oxidising agent, the ferric oxide film escapes destruction; presumably any cathodic action would reduce chromic acid in preference to ferric oxide.

It would seem likely that high-pressure oxygen (such as can be obtained by anodic action under conditions where there is appreciable oxygen overvoltage) might prevent the destruction of the films, acting like chromic acid. If, however, the film contains a metal, such as chromium, whose tervalent ions are not easily reduced (Latimer, " Oxidation Potentials," Prentice-Hall, 1938), ordinary (low-pressure) oxygen dissolved in the acid might suffice. It is possible that the invisible film on stainless steel is protected in this way by low-pressure oxygen, which prevents reductive dissolution, allows the film to be repaired at gaps, and to be thickened at points rich in lattice defects; austenitic stainless steel resists dilute sulphuric acid in the presence of oxygen, but not in its absence—a matter now under experimental study.

A heat-tinted iron electrode, plunged into dilute sulphuric acid, in such a way that it is subjected to anodic action from the instant of immersion, immediately becomes passive, provided the current density is sufficiently high; oxygen is evolved, the interference colours remain unchanged, and the iron is practically unattacked (Evans, *J.*, 1930, 482). If the current is interrupted for more than a few seconds, the film is destroyed and the colours disappear; when the current is again turned on, the iron behaves as an active anode, passing easily into solution. A very short interruption is, however, possible without loss of passivity or destruction of the film. In the experiments of 1930, the period of interruption which could be tolerated without loss of passivity seemed to increase with increase of time of current flow—as though the oxide film had become more protective as the anodic treatment was prolonged; however, the relationship was not studied.

The temporary immunity obtained after short interruptions may tentatively be attributed to the oxygen-charge left by the anodic treatment, since oxygen should suffer reduction before the ferric oxide itself is destroyed. If so, a detailed study of the phenomenon might give information useful in the study of the immunity of stainless steel, where traces of oxygen in the liquid suffice to maintain passivity. Hence, the present research was undertaken into the relation between the time of current flow (t_c) and the time of auto-reduction or breakdown of the film (t_b).

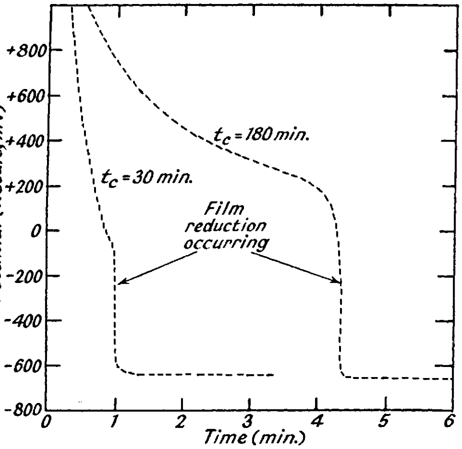
EXPERIMENTAL

Materials.—Swedish iron sheet, 0·16 mm. thick, was used, containing C, 0·034%; Si, 0·010%; Mn, 0·145%; S, 0·015%; P, 0·032%; Ni, 0·030%; Cr, 0·007%; Mo, 0·005%; V, 0·010%; Ti, 0·010%; Al, 0·006%; Sn, 0·006%; W, 0·050%; Cu, 0·010%; Pb, 0·001%. It contained plentiful inclusions of magnetite (Evans, *Nature*, 1949, **164**, 909.)

Preparation of Specimens.—Pieces of iron measuring 1·4 × 3·0 cm. were degreased in benzene, the excess being taken up with filter-paper, abraded with 3/0 emery paper, again degreased, and dried. The specimens were heated in an electric air-oven, being supported in a rack made by cutting slots in an aluminium block 20 × 2 × 2 cm. The iron specimens rested in the slots so that they remained freely accessible to the air and all at the same temperature; a " Sunvic " thermo-electric regulator was used to maintain the oven at 235° ± 2° and the specimens remained at this temperature for 34 hours. A first-order dark-blue interference colour was produced evenly over the whole area—suggesting a uniform film-thickness; the film thus obtained is largely composed of rhombohedral α-ferric oxide (Winterbottom, *J. Iron Steel Inst.*, 1950, **165**, 9; Pryor and Evans, *J.*, 1950, 1259; "Chemistry Research," 1950, D.S.I.R., Teddington). After cooling, part of each specimen was masked with polystyrene, dissolved in xylene, and then a layer of paraffin was applied molten, in order to protect the water-line zone; an area of oxide 1·4 × 1·4 cm. was left exposed on each side.

Apparatus.—A tinted specimen served as anode, and an untinted piece of iron as cathode. Before the experiment they were both clamped to a frame consisting of two parallel strips of fibre rigidly connected together (Evans, *J. Soc. Chem. Ind.*, 1928, **47**, 73T, illustration). The anode and cathode were connected by flexible wire through a variable resistance, key, and milliammeter to accumulators; the distance between the two electrodes was 3·0 cm. When the frame was lowered, the current flowed from the instant when the electrodes entered the acid.

FIG. 1. *Typical time–potential curves obtained after interruption of current.*



0·1M-*Sulphuric acid; C.D.* 6 *ma/sq. cm.; temperature* 6°±1°.

FIG. 2. *Diagram of apparatus used for measuring the variation of* t_b *with* t_c.

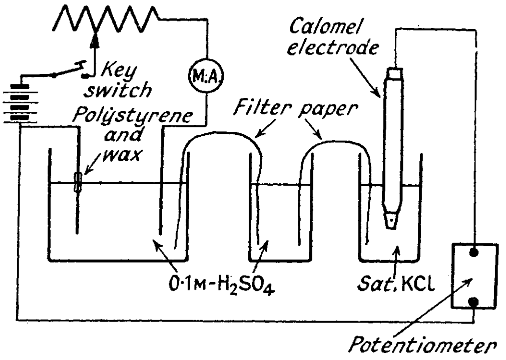


FIG. 3. *Relationship of* t_b *and* t_c; *C.D.* 6 *ma/sq. cm.*, 0·1M-*sulphuric acid at* 6°.

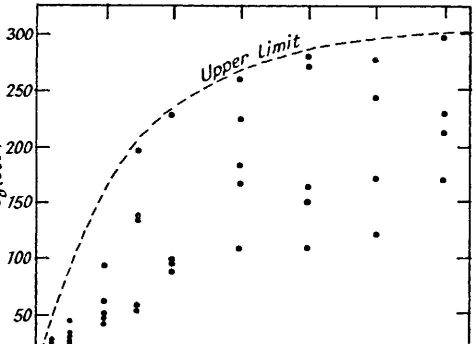
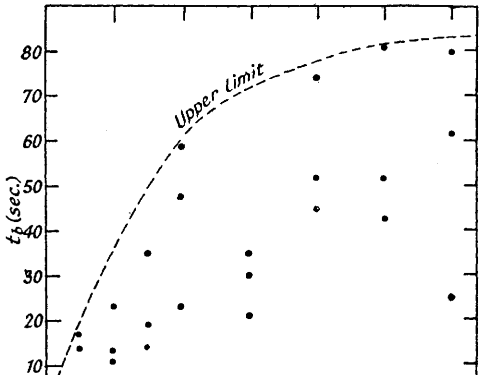


FIG. 4. *Relationship of* t_b *and* t_c; *C.D.* 6 *ma/sq. cm.*, 0·1M-*sulphuric acid at* 24°.



Method.—The time of breakdown of the film after a certain period of anodic treatment was measured by a method involving changes in the single-electrode potential of the iron. Fig. 1 shows typical time–potential relationships for two specimens after the current which had previously flowed for 30 and 180 minutes, respectively, had been interrupted. The single-electrode potential of iron changes sharply when the oxide film is reduced, dropping some 700 mv within a second. If the polarising current is restarted before the sudden drop, the electrode remains passive and oxygen is again evolved; if it is restarted after the drop, the iron corrodes actively and no oxygen appears. The sudden drop also corresponds with the disappearance of the interference colour.

The circuit used is shown in Fig. 2. Potential measurements were made with a valve-potentiometer against a saturated calomel reference electrode in saturated potassium chloride. The potentiometer was adjusted to a potential reading of −400 mv, a value slightly above that of active iron. In each experiment the specimen was polarised anodically in 0·1M-sulphuric acid for a known period of time (t_c), and then the polarising current was interrupted. When the film suffered auto-reduction, the needle of the potentiometer swung across the scale and the time between the interruption and the swing was taken to correspond to the time of breakdown (t_b).

Results.—(1) *Dependence of* t_b *on* t_c. Two series of experiments were carried out in which the t_b values for specimens anodically polarised for periods ranging up to 360 minutes were measured. In both, 0·1M-sulphuric acid containing dissolved oxygen was used; the temperature of the acid was maintained at 6°±1° in the first series and at 24°±1° in the second. The polarising current density, based on apparent area, was kept constant at 6 ma/sq. cm. in each case. The results are shown in Figs. 3 and 4.

The time of breakdown increases significantly with increasing time of anodic pretreatment. There is, however, a wide scatter of t_b values for any given t_c time. Despite the scatter, there appears to be an upper limit to the t_b value possible for any given t_c. The upper limiting value of t_b increases with t_c, the curve being roughly asymptotic. It seemed possible that the low and the high values might be given by specimens coming from different parts of the original iron sheet from which the specimens had been cut; an enquiry into this matter showed no correlation between the t_b values and position on the original sheet.

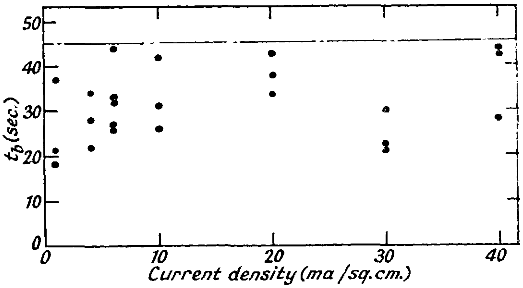


FIG. 5. *Values of* t_b *after* 30 *mins.' polarisation at various current densities, in* 0·1M-*sulphuric acid at* 6°.

(2) *Effect of temperature.* The increase of t_b with t_c is significant at both the temperatures studied and the shapes of the " upper limiting " curves are similar. However, the t_b values obtained at 24° for any given t_c are considerably lower than the t_b values obtained at 6°. The increase in auto-reduction rate with temperature confirms earlier observations (Pryor and Evans, *J.*, 1950, 1259).

(3) *Effect of current density.* A series of experiments were carried out in order to discover whether the current density used for the anodic polarisation affects the time of breakdown. The t_c period was fixed at 30 minutes and, 0·1M-sulphuric acid being used at 6°±1°, the t_b values were measured for apparent current densities ranging from 1 to 40 ma/sq. cm. Specimens introduced at current densities below 1 ma/sq. cm. suffered auto-reduction at once. The results are shown in Fig. 5 and indicate that t_b does not increase with increase in the current strength during the t_c period.

DISCUSSION

During anodic treatment, the blue interference colour of the α-ferric oxide changes to a pale yellow after a t_c period exceeding approximately 2 hours. When the current is interrupted after such a t_c time, the colour of the specimen changes uniformly and rapidly as auto-reduction occurs; the colour of the specimen first darkens to the original blue and then the whole sequence of first-order tints appears in the reverse order as film-thinning proceeds. Apparently some slow film-thickening is occurring during the anodic polarisation, the pale colour just mentioned corresponding to a film giving the second-order yellow.

In the absence of applied current, auto-reduction of the oxide film is due to local cells

Fe|acid|Fe_2O_3. The anodes are points in the film where metal cations can readily pass through, either because the film is thin or because it is in a state of atomic disarray; the thin places may be the sites of old cracks which have been partly healed. Whilst the specimen is undergoing anodic treatment with evolution of oxygen, any cations emerging at sensitive points are arrested and used to provide oxide for film repair, as in dry oxidation. Any fresh defects are blocked with oxide as they appear—explaining the slow thickening of the film. When, however, the current has been interrupted any fresh discontinuities will permit cations to enter the liquid, and this anodic reaction must be accompanied by cathodic destruction of the film at points immediately adjacent, so that the discontinuity spreads rapidly.

α-Ferric oxide is believed to be a semi-conductor of the metal-excess type, containing vacant sites in the oxygen lattice (Pfeil, *J. Iron Steel Inst.*, 1929, **119**, 501; **123**, 237; Garner, *Chem. and Ind.*, 1947, 132; Bevan, Shelton, and Anderson, *J.*, 1948, 1729). It has been further shown that the composition of the oxide varies with the effective oxygen pressure of the phase with which it is in contact; probably, during prolonged anodic treatment with oxygen evolution, the outer portion of the film will acquire an oxygen content considerably higher than that of similar oxide which has not experienced anodic pretreatment. On interruption of the current, the excess of oxygen must be removed from the whole surface by cathodic action before the localised reduction of the oxide proper can occur close to the discontinuities. This must be the case since the potential of the ferric oxide containing excess of oxygen exceeds that of the ferric oxide which has lost most of its excess (see Fig. 1). When once the excess of oxygen has been exhausted, the reductive dissolution of the oxide itself will start and this will be localised owing to considerations of resistance, so that the area of bare metal will rapidly increase. Thus film-destruction, once started, is self-stimulating.

The charge of excess of oxygen will become greater with increasing t_c and, therefore, t_b will also increase with t_c. The content of excess of oxygen in the film is apparently limited. (It may, for instance, be determined by the number of vacant anion sites near the surface. Once these sites have been filled, replenishment by the diffusion of vacant sites from the interior of the oxide to the surface will be very slow at the temperatures under consideration. Provided the rate of anodic oxygen discharge is ample to fill the vacant sites as they reach the surface, the value of the current density should be unimportant—thus explaining the results of Fig. 5.) After a certain time of anodic treatment, the greatest possible oxygen charge will be approached. Thus, there is a limiting value of t_b which can never be exceeded, explaining the asymptotic shape of the curves in Figs. 3 and 4.

The scatter of t_b values obtained at a fixed t_c value remains to be explained. It was observed that all the films were immediately reduced if touched with an iron wire. Hence the premature destruction of the oxide films on certain specimens may be accounted for by the formation of an actual crack in the film, sufficient to allow acid to come into contact with metallic iron. Such cracking is not improbable. Earlier work (Evans, *Nature*, 1946, **157**, 732) has indicated the presence of weak points in films formed at low temperatures in air; they were repaired by fresh oxidation but others are continuously and spontaneously appearing. Presumably the defects arise from internal stresses, the presence of which is suggested by the wrinkling or curling when the films are transfered to vaseline-coated glass (Evans, Symposium on Internal Stresses in Metals and Alloys, Inst. Met., October 1947, p. 291). The irreproducibility of the results is an indication that the disastrous cracking occurs only at intervals wide in time and space. If the number of cracks to be expected in a specimen area during a time typical of t_b were large, Bernouilli's principle would predict reproducibility. Any such cracks occurring during the t_c period would be repaired without the reductive destruction of the main film. Even a crack formed just after interruption of the current might be repaired, since there would still be a high oxygen charge in the outer layers of the oxide and dissolved oxygen in the acid. This is suggested by the fact that few points are found in the lower half of the area below the limiting curve. But any crack produced during the period of interruption, which cannot be repaired by oxygen existing in or around the oxide film, causes rapid and self-stimulating autoreduction.

The interpretation offered above is advanced tentatively, but it appears to cover the facts.

Conclusions.—The oxide film on iron is immediately auto-reduced by dilute sulphuric acid; anodic polarisation preserves the film and oxygen is evolved. During the anodic treatment, the film acquires a charge of excess of oxygen in its outer layers which (like chromic acid in earlier work) must be removed from the whole surface before localised reduction of the ferric oxide can start. Scatter of the results is attributed to periodic cracking of the film which causes premature auto-reduction.

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