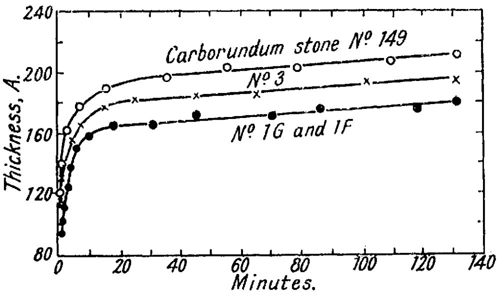
263. *The Passivity of Metals. Part VIII. The Rate of Growth of Oxide Films on Iron.*

By H. A. Miley and U. R. Evans.

An electrical method of estimating oxide films, previously checked by comparison with optical and gravimetric determinations, has been used to obtain time–thickness curves, which show that even at the ordinary temperature the oxidation of iron in dry air is very rapid. The parabolic law is not in general obeyed. Combining the new observations with those of other authors, it appears that the film responsible for the colours on heat-tinted iron is α-Fe_2O_3 above 200°; above 400° this is backed by magnetite, and above 575° a third layer, essentially ferrous oxide, appears. Probably the film formed below 200° is γ-Fe_2O_3.

The invisible oxide formed on unheated iron during exposure to air can play an important part in predisposing the metal to passivity. W. J. Muller and Machu (*Sitzungsber. Akad. Wiss. Wien*, 1932, **141**, 279; *Z. physikal. Chem.*, 1932, *A*, **161**, 411) found that the " time of passivation " of iron after air-exposure was only 1/20,000 that of iron in the film-free state. One of the authors has shown that pre-exposure to air reduces the probability of attack or depresses the number of starting points of corrosion in certain liquids (Evans, J., 1927, 1030; Mears and Evans, *Trans. Faraday Soc.*, 1935, **31**, 532; Britton and Evans, *Trans. Electrochem. Soc.*, 1932, **61**, 446); pre-exposure to air has, however, little effect where the liquid is strongly corrosive or where it can itself produce passivity. Early film-stripping experiments suggested that the growth of the film was rapid (Evans, J., 1927, 1029); probably the ragged films obtained by stripping iron immediately after abrasion originate in the intense but transitory heating which accompanies all abrasion, as indicated by Bowden and Ridler (*Proc. Roy. Soc.*, 1936, *A*, **154**, 640); but the fact that iron exposed to air before stripping yields more continuous flakes points to a relatively rapid filling in of the larger discontinuities in the ragged film, although air-formed films never become " protective " in any general sense. The same rapidity of oxidation was indicated optically by Freundlich, Patscheke, and Zocher (*Z. physikal. Chem.*, 1927, *A*, **128**, 321; 1927, **130**, 289) and by Tronstad and Höverstad (*ibid.*, 1934, **170**, 172). The electron-diffraction work of Dobinski (*Nature*, 1936, **138**, 31; *Phil. Mag.*, 1937, **23**, 397) indicates that metal polished in air is heavily oxidised (on metal polished below benzene or pentane no oxide was detected, although it appeared on subsequent exposure to air). Similar results have been obtained by Nelson (*Nature*, 1937, **139**, 30; *J. Chem. Physics*, 1937, **5**, 252) and by Preston and Bircumshaw (*Phil. Mag.*, 1935, **20**, 706); Iitaka, Miyake, and Iimori (*Nature*, 1937, **139**, 156) have applied electron-diffraction study to the films produced on iron by air or by chromate, after stripping by the method of Evans (J., 1927, 1022), and have confirmed several of his conclusions.

FIG. 1.



Oxidation of iron in a desiccator at 18° *after different abrasions.*

Vernon thinks that his weight–time curves (*Trans. Faraday Soc.*, 1935, **31**, 1676) indicate a much slower oxidation rate, but Price (unpublished work) considers that Vernon's results are consistent with the views expressed above.

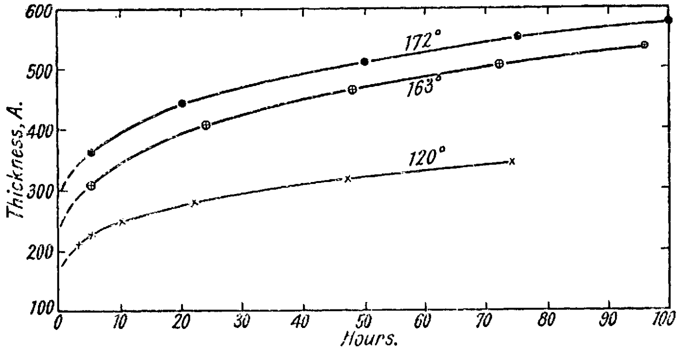
Evidently a full understanding of passivity demands a knowledge of the rate of formation of oxide on iron during air exposure. Since gravimetric measurements of oxidation require knowledge of the amount of oxide present at the time of the first weighing, an electrometric procedure has been developed, depending on the number of millicoulombs needed to reduce the film from the ferric to the ferrous state. A similar principle had been applied to measure silver iodide films, where it agreed with gravimetric and iodometric measurements (Evans and Bannister, *Proc. Roy. Soc.*, 1929, *A*, **125**, 380), whilst for oxide films it has been found to agree both with optical results, and with gravimetric results when corrected for the original oxide (Evans and Miley, *Nature*, 1937, **139**, 283). The experimental method described by one of the authors (Miley, *Carnegie Schol. Mem.*, 1936, **25**, 197) was adopted, ammonium chloride being used as the electrolyte, together with a constant current, so that a measurement of time alone sufficed to indicate the millicoulombs needed for the cathodic reduction of the ferric oxide (insoluble in ammonium chloride) to ferrous oxide (which dissolves readily).

Throughout this paper, the word " thickness " denotes the *mean general intercept*, *i.e.*, the average of the intercepts made by the film on a large number of parallel lines drawn at right angles to the *general* plane of the surface.

Materials.—Iron, prepared from the carbonyl and of German origin, rolled to thickness of 0·38 mm., was employed. This is almost free from metallic impurities, and usually contains $< 0{\cdot}03\%$ of carbon. The sheet was coarse-grained and probably not quite free from porosity. The standard finish consisted of grinding with French emery No. 1G, finishing with No. 1F, and washing with benzene. In some experiments for comparative purposes the specimens were ground with French emery No. 3 or with a carborundum stone No. 149. In the low-temperature experiments, the specimens were kept in a desiccator filled with calcium chloride and soda–lime in a room kept at 18° by a thermostat. Some experiments at higher temperatures were carried out in a thick-walled electric furnace of high heat capacity. The specimens were kept at the required temperature for different times, and the oxide present estimated electrically.

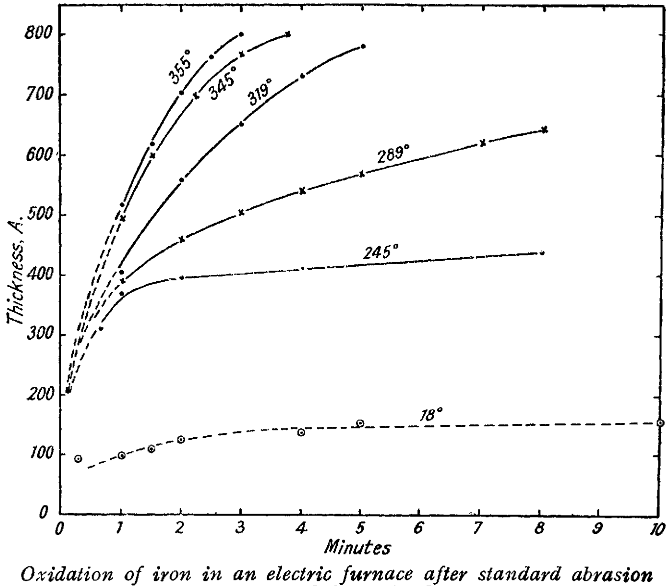
Results.—The time–oxidation curves are shown in Figs. 1, 2, and 3. They confirm the view that, even at ordinary temperatures, oxidation is a rapid process. The rate of oxidation decreases as the oxide produced accumulates, but there appears to be no limiting thickness; the experiment at 163° was continued for 25 days, and the thickness was still increasing. The usual parabolic law connecting mean film-thickness (y) and time (t), *viz.*, $dy/dt = k/y$ or $y^2 = k't + k''$, was not in general obeyed. This is not surprising, since the physical basis of the law (often valid for thick films and high temperatures) requires a film thick compared with the corrugations and disorganised layer of the surface—a condition which is absent on the specimens studied.

FIG. 2.



Oxidation of iron in an electric furnace after standard abrasion.

FIG. 3.



Oxidation of iron in an electric furnace after standard abrasion (broken curve obtained from the data of Fig. 1).

Composition of the Film.—Early film-stripping work (Evans, J., 1927, 1027) suggested that the films produced at lower temperatures consisted only of ferric oxide, but that at somewhat higher temperatures, a magnetite layer appeared below the ferric oxide; the interference colours were determined by the thickness of the ferric oxide layer. Pfeil (*J. Iron Steel Inst.*, 1929, **119**, 501; 1931, **123**, 237) found that, immediately below 575°, there were two layers (ferric oxide and magnetite), whilst above 575° a third layer appeared (essentially ferrous oxide but containing more oxygen than corresponds to the formula FeO).

During the electrical estimations of film-thickness mentioned above, it was noticed that metal oxidised below 375° became clean and bright after the cathodic reduction; but if the metal had been tinted above 400° there remained, after the removal of the colour film, a black deposit on the metal surface, evidently the magnetite present at the base of the ferric oxide. To ascertain whether the outer " colour-film " was really ferric oxide, certain specimens were tinted, washed in water, alcohol, and ether, dried in a vacuum, weighed, and then subjected to cathodic reduction for a time *insufficient* to reduce the oxide completely; after being again washed and dried they were reweighed. A comparison between the weight-loss measured directly and that calculated from the millicoulombs on the assumption that the film is ferric oxide and becomes reduced to the ferrous state shows good agreement (see table); numbers calculated on the assumption that the film was magnetite would have been 1·47 times greater. Evidently the colour-film is ferric oxide, not magnetite.

Comparison Between Millicoulombs Expended and Weight-loss (in mg./dm.^{2}).

Weight-loss (calc. from millicoulombs)	0·63	0·59	0·62	0·56	0·95	0·98	0·92	0·90
Weight-loss (gravimetric)	0·61	0·57	0·63	0·54	0·96	0·95	0·89	0·86

This quantitative relation was not found for films produced below 200°. Vernon (*Trans. Faraday Soc.*, 1935, **31**, 1674) had previously noticed differences in the films formed below and above 200°; amounts of oxide, which, if produced above 200°, would have sufficed to give colours, produced no colours when formed below this temperature. This fact was also confirmed when electrical estimation was employed. Preston and Bircumshaw (quoted by Vernon) found, by electron diffraction, that oxide formed below 200° was either γ-ferric oxide or magnetite, whereas above 200° it was α-ferric oxide. Iitaka, Miyake, and Iimori (*loc. cit.*), after determining by electron diffraction the structure of the films formed at ordinary temperatures and stripped from the metallic basis, concluded that they were either γ-ferric oxide or magnetite. They then performed chemical tests which decided in favour of the former.

If the Japanese authors' conclusions are accepted, the abnormally low weight-loss suffered by specimens tinted below 200° on partial reduction in ammonium chloride can be tentatively explained by assuming that ferrous oxide from γ-ferric oxide is not as quickly soluble in ammonium chloride as is that from α-ferric oxide. This is supported by the observation that these specimens gain in weight on subsequent exposure to air, reaching a constant value—presumably when the residual ferrous oxide has become completely reoxidised. Specimens tinted above 200° do not show this weight increase.

It seems, therefore, fairly certain that the thin films formed on iron in air are : Below 200°, one layer, γ-Fe_2O_3; between 200° and 400°, one layer, α-Fe_2O_3; between 400° and 575°, two layers, α-Fe_2O_3 and Fe_3O_4; above 575°, three layers, α-Fe_2O_3, Fe_3O_4, and " FeO."

THE METALLURGICAL LABORATORIES, CAMBRIDGE UNIVERSITY. [*Received, June 16th*, 1937.]