The Passivity of Iron.

By U. R. EVANS.

IN 1790, James Keir¹ discovered that treatment of iron with nitric acid produces a peculiar condition in which the metal loses its power of precipitating silver from silver nitrate, although retaining its 'metallic splendour'. The behaviour of iron towards nitric acid was further examined by Schönbein² and Faraday;³ Schönbein described the peculiar condition as 'passivity'. Later work has shown that many other oxidising agents render iron passive towards reagents which attack the metal in its ordinary or 'active' condition; reducing agents tend to restore 'activity'. Similarly, anodic treatment may produce passivity, but cathodic treatment usually renders the metal active again. Low temperatures favour continuation of passivity, and high temperatures a return to activity; alkalis are favourable to passivity, and non-oxidising acids to activity. These facts cannot fail to suggest that passivity is due to a protective oxide film.

The objection has been raised that passivity can be produced under conditions where an oxide film would be dissolved. Recent work, however, has shown such statements to be untrue. Furthermore, the oxide films responsible for the principal types of passivity have now been stripped from the metal and studied; although invisible when in optical contact with the bright metal, the films are perfectly visible when lifted from it. Finally, optical methods have been worked out which enable the invisible film to be detected whilst still upon the metal; such methods depend on the manner in which a film affects the character of polarised light reflected at a metallic surface—a subject examined mathematically by Drude.⁴ The cause of passivity is therefore no longer in doubt, and the time is appropriate to review the subject.

PASSIVITY DUE TO NITRIC ACID.

Dilute nitric acid consumes iron far more rapidly than dilute sulphuric acid; but the concentrated acid produces only a feeble reaction, and even this soon dies away, the iron becoming passive; the iron may then be brought into acid sufficiently dilute to attack active iron, and yet will remain unchanged. It has been alleged that this type of passivity cannot be due to a layer of oxide, which, it is argued, would be destroyed by the acid. In 1928, however, Hedges⁵ studied the action of nitric acid on ferric oxide (free from hydroxide), and found that there was practically no dissolution at low temperatures; when the acid was heated, dissolution set in at about 75° C., and this is roughly the temperature at which the passivity of iron, placed in nitric acid, breaks down. Thus, Hedges not only removed the objections to the oxide film view, but also produced new evidence in its favour. I have found it possible to keep flaky ferric oxide in nitric acid for six days without destruction of the flakes.⁶ The film formed on iron by concentrated nitric acid is invisible, but, in 1900, Michéli⁷ obtained optical

evidence of its existence. Moreover, Benedicks and Sederholm⁸ have shown that iron placed in dilute nitric acid containing alcohol develops a film which displays a network of cracks on drying; in this special case, therefore, the film becomes visible even when it is still attached to the metal. There is no reason to doubt that the passivity produced by nitric acid is due to an obstructive film of ferric oxide.

PASSIVITY PRODUCED BY EXPOSURE TO AIR.

Pilling and Bedworth⁹ have divided metals into two classes, according to the relation between the densities of the elements and their oxides. In the first class, the natural volume of the oxide is less than the volume of the metal needed to produce it; here any superficial oxidation will necessarily produce an oxide layer pierced by voids through which oxygen can pass unobstructed to attack the metal below. This class includes most of the lighter metals, such as magnesium and calcium, and it is not surprising to find that those metals 'burn' readily in air. Iron and most other heavy metals belong to the second class. Here, the oxide, when unstressed, occupies a greater volume than the metal contained in it. Consequently, conversion of the surface into oxide will produce a layer free from voids, which is actually in a state of lateral compression.

At ordinary temperatures, such a film, even when very thin, should exclude oxygen from the metal below, and thus the film on iron exposed to dry cold air never attains 'visible thickness'. At slightly elevated temperatures, diffusion of oxygen through the solid film becomes possible, and the film may reach a thickness comparable to the wavelength of light, so that interference tints appear on the metal; at still higher temperatures, a thick greyish scale is produced, which often tends to crack and peel off.

This cracking and peeling is very characteristic of relatively thick films. It is partly attributable to differences in the coefficients of expansion of iron and its oxide; but probably even if produced and held at constant temperature, a thick film would tend to crack more than a thin film. All films formed on heavy metals must possess potential energy due to the state of compression, which energy will be released when the film becomes detached. Thus, the work needed to detach area a of an ideal film of thickness θ will not be less than $aW_A - a\theta P_c$, where W_A is the adhesional work per unit area and P_c the compressional energy per unit volume (work against cohesive forces is neglected, being small for a thin film). When, therefore, the thickness θ is less than W_A/P_c , energy must be expended in stripping the film; but if the thickness is greater than that value, spontaneous peeling is at least not impossible. In the case of scale produced at a red heat, this spontaneous detachment can often be observed microscopically, whilst the

ultra-microscopic cracking of films of the interference colour range is inferred from the fact that these films have a far smaller protective action than 'invisible' films, which are too thin to give colours. Electrolytic iron, if freshly abraded, quickly precipitates copper when a drop of dilute copper nitrate solution is placed on the surface. If the iron is exposed to air at ordinary temperatures for some time before the copper nitrate is applied, the deposition of copper does not occur; the time needed for the formation of a film sufficiently continuous for protection is much greater after coarse abrasion than after fine abrasion, doubtless owing to the internal stresses and ultra-microscopic fissures left in the metal in the first case. If the iron is gently warmed in air and cooled again, the passivity towards copper nitrate is produced more quickly than at ordinary temperatures; but if the warming has been conducted at temperatures where interference tints appear, deposition of copper commences, starting at points representing cracks in the film. Thus, if a strip of freshly abraded iron is gently heated for a few seconds at one end (the other end being unheated), cooled and tested with copper nitrate, the iron will usually be found active at the unheated end, where the film is incomplete, and also at the heated end, where it is cracked; but there will generally be a passive region in the gently warmed part in the middle.

There is little doubt that the nitrate itself has some film-repairing action, since copper sulphate usually produces some deposition of copper under analogous conditions. Copper chloride invariably produces instantaneous growth of copper; chlorine ions can penetrate through imperfections which the larger ions cannot pass.¹⁰ Even in copper nitrate the passivity of iron often tends to break down at jagged places. This failure is to be expected; geometrical considerations indicate that, at points of high convex curvature, the metallic atoms will, on oxidation, move outwards to a circle of greater radius, so that the lateral compression already referred to will be abnormally low at these points.

Steel or commercial iron does not attain reliable passivity on exposure to air alone; the junction between dissimilar phases constitutes a place where a protective film is liable to break down. But if steel is treated in a solution of chromic acid or potassium chromate the weak places are brought into repair, and a drop of copper nitrate afterwards produces no action.

In recent papers which I have published,¹¹ with J. Stockdale, L. C. Bannister, S. C. Britton, and other collaborators, methods are described for isolating oxide films from a metallic basis. All methods depend on an operation, such as immersion in iodine, or anodic treatment in a chloride or sulphate solution, which dissolves the metal just below the oxide film; this allows the oxide film to peel off or to be transferred to glass or cellophane. In the case of some metals, particularly nickel, the films responsible for heat-tints themselves show bright colours after removal. The protective films on iron made passive by exposure to air at low temperatures, being too thin to give colours, are invisible

whilst on the bright metallic surface; but they are found to be plainly visible when removed from it. Being thinner than the films from heat-tinted iron, they are, as a whole, more transparent; but since there is more interlocking with the metal when the film is thin, the 'passivity films' show frequent opaque spots due to residual metal. A comparative study of films above and below the limiting thickness needed to produce colour (about 400 Å.) has indicated that no sharp change of properties occurs at the limiting thickness, the position of which is merely fixed by the accident that the human eye is insensitive to waves below a certain wave-length.

The thinner (invisible) films have been detected optically whilst still on the metal by Freundlich, Patscheke, and Zoher,¹² whose conclusions agree with the results of the Cambridge experiments in indicating that combination of iron with oxygen occurs rapidly even at room temperature, although the films cease to grow before they reach visible thickness.* A pure iron mirror free from oxide was obtained by heating iron carbonyl vapour in a closed vessel. When air was admitted and quickly pumped out again, an oxide film was left on the metal which could be detected by the polarised light method; simultaneously the mirror became inert to nitric acid of specific gravity 1.4, although similar mirrors not exposed to air were attacked by the acid under identical conditions. The optical change corresponded to a mean film-thickness of about 10 Å. The films produced on abraded surfaces at Cambridge are very much thicker, since the abrasion produces a zone of disorganised metal, and the oxygen can penetrate more deeply. These thicker films are actually less protective than the very thin ones; but to the experimenter the thickness is useful, since it allows the film to be removed from the metal.

PASSIVITY PRODUCED BY ANODIC TREATMENT.

The fact that an iron anode becomes passive in an alkaline solution is easily understood on the oxide film view. But anodic passivity can also be produced in a neutral salt solution, or even (if the current density is high enough) in dilute acid. When iron is made the anode in dilute sulphuric acid at a low current density, it passes smoothly into solution as ferrous sulphate. When the initial current density is high, dissolution also occurs normally at first; but later passivity sets in, the dissolution slows down, and the current sinks to a lower value. The current, which continues to flow in the passive state (providing the e.m.f. is high enough), is mainly devoted to the production of oxygen gas; the dissolution of iron, although still measurable, becomes very slow.¹³

W. J. Müller¹⁴ has shown that the time needed to produce passivity becomes shorter as the initial current density is increased; he has also demonstrated that passivity never sets in until the liquid layer next to the metal has become saturated with

* Some evidence of the very rapid oxidation of iron in air at low temperatures was provided by Faraday in his "Experimental Researches in Electricity", Series XVII. § 2049 (1840). I am indebted to Mr. A. Marshall for directing my attention to this work.

some iron compound; indeed, at this stage the polarising microscope has revealed some solid substance, apparently $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, upon the metallic surface.¹⁵ It is unlikely, however, that a layer of ferrous sulphate is directly responsible for the passivity; ¹⁶ for all visible material present on the iron surface peels off or disappears when complete passivity sets in, a circumstance noticed by Hedges.¹⁷ When once oxygen evolution has begun, the metal is clean and bright, and the passivity is certainly due to an invisible oxide film on the surface. This film has recently been detected and measured optically in an important research by Tronstad,¹⁸ who has followed the increase of film thickness under anodic treatment, as well as the diminution under cathodic treatment, in acid, neutral, and alkaline solutions.

Probably authorities would still differ regarding the details of the anodic reactions. When the iron is active, the discharge of sulphate ions to give ferrous sulphate may conveniently be written thus:

The ferrous sulphate will at first dissolve in the liquid, regenerating $\text{SO}_4^{''}$ ions; but at high-current densities the liquid layer will soon become supersaturated, and solid matter will separate out, covering up most of the surface, and raising the true current density on the small part still uncovered. This may permit the local potential to rise high enough for the inception of alternative reactions, which absorb greater amounts of energy. For example, the discharge of hydroxyl ions, according to the equation

becomes quite possible at this stage, since the hydrogen ion concentration of the layer next the anode is now greatly decreased. The oxygen may convert the iron superficially into oxide, which will interfere with further conversion of iron to sulphate; but the major part of the oxygen will stream off as oxygen bubbles, which will dissipate the visible crust of ferrous sulphate or basic salt, and leave only the invisible oxide to protect the metallic surface.

I have investigated the objection that sulphuric acid would dissolve a ferric oxide film,¹⁹ commencing by studying iron covered with a visible ferric oxide film. Iron heated in air to give an early interference tint (caused by a film of 500-800 Å. thickness) was cooled and introduced into *M*/10 sulphuric acid; within a second, the film was dissolved away and the colour vanished. The experiment was repeated with iron heated to give thicker films (greater than 2000 Å.); here there was some slight attack at first, but the films soon peeled off, and, as soon as the oxide was out of contact with the metal, the dissolution practically ceased; the film flakes could then be collected, washed, and photographed. This shows that sulphuric acid has practically no *direct* action on ferric oxide; the rapid destruction of the film in contact with metal is due to the cell

Iron | Sulphuric Acid | Ferric Oxide

set up at discontinuities; the ferric oxide is the

cathode of this short-circuited cell, and becomes reduced to ferrous oxide, which at once dissolves in the acid; it seems that oxides of the type MO are usually much more quickly attacked by acid than those of the type M_2O_3 . This explanation is supported by the fact that if chromic acid, a strong oxidising agent, which would prevent the reduction, is added to the dilute sulphuric acid, heat-tinted iron can be kept in the acid mixture for many hours without loss of colour.

Heat-tinted iron was then subjected to anodic treatment in *M*/10 sulphuric acid (the e.m.f. and resistance being such as to provide a current density of 6 amp./dm.² when the iron was active, or 3 amp./dm.² when it was passive). It was found that if the tinted iron was introduced into the acid before the circuit was completed, the colour film was destroyed, and when the current commenced to flow, the iron behaved as an active electrode, passing into solution as ferrous sulphate. But if the circuit was completed before the introduction of the anode, so that the current flowed from the instant of immersion, then the iron was passive from the first moment, and oxygen was evolved, the colour due to the film remaining undestroyed. It was then possible to interrupt the current for a few seconds without destruction of the film; during the interruption a few oxygen bubbles continued to rise from the metal, indicating a residual charge of excess oxygen, which doubtless prevented the local reduction to the quickly soluble ferrous compound. If the circuit was restored before this supercharge of oxygen was exhausted, the iron was still found to be passive, oxygen was again evolved freely, and the colour remained undestroyed. But if the interruption was continued after the bubbles representing the supercharge had ceased to appear, then the oxide film was destroyed by the mechanism already indicated, the colour vanished, and, on restoring the circuit, the iron was active, and dissolved freely without any appearance of oxygen. If the circuit was restored at the precise moment when the film had suffered destruction at some points but not at others, dissolution of the iron commenced at the film-free points, thence extending under the skin, which peeled off in curling flakes. When once these oxide flakes had passed out of contact with the metal, their dissolution ceased.

Experiments conducted on iron which had been exposed, after abrasion, to air at ordinary temperatures showed remarkable analogies with the results obtained on heat-tinted specimens; evidently, the thin invisible films behaved in much the same way as the thicker colour-films. When the current was turned on after the anode entered the acid, the iron was dissolved freely, whereas if the circuit was completed before the introduction of the anode, the iron was usually passive from the moment of immersion, oxygen being evolved from the surface. The current could then be interrupted for a few seconds without destroying the passivity, but if the interruption was prolonged beyond the short period during which the slow stream of oxygen bubbles (representing the supercharge) rose from the metal, then, on restoring the current, the iron behaved as

an active anode, and iron passed freely into solution without evolution of oxygen. Special experiments,²⁰ in which the circuit was restored at a chosen moment when the film was destroyed at certain points but not at others, indicated that it was possible to undermine the invisible film formed during the previous passive period; it peeled off in curling microscopic flakes, which, although mechanically flimsy, were chemically stable in the acid, when once out of contact with metallic iron. Thus the films responsible for anodic passivity, like those responsible for air-passivity, have been stripped from the reflecting basis and rendered visible.

Space does not permit the discussion of several other aspects of anodic passivity, particularly the periodic alternations between the active and passive states which often occur at a range of current densities intermediate between the activity and passivity ranges. For this matter, the reader is referred to the work of Hedges,²¹ who has made the subject particularly his own.

CONCLUSIONS.

It is not suggested that all inert metals owe their lack of reactivity to oxide films; metals like gold will react very slowly even when quite free from films. But the important types of passivity in iron are almost certainly due to films of ferric oxide. The facts as known to-day confirm in many respects the porous oxide film theory put forward twenty-five years ago by Haber and Goldschmidt.²² All iron which has been exposed to air is covered with an oxide film; the essential difference between active iron and passive iron is that on the former the film is in bad repair and on the latter it is in good repair; the degree of initial repair needed to

cause a sample of iron to display passivity will vary with the presence or absence of film repairers or penetrating ions in the solution into which it is to be introduced. A ferric oxide film will only resist the action of a non-oxidising acid, for example, dilute sulphuric acid, if a supercharge of oxygen is present to prevent local reduction to the rapidly dissolving lower oxide, or alternatively if an oxidising agent, for example, chromic acid, is also present; where the main acid is itself an oxidising agent, for example, nitric acid, this reduction does not occur.

I am indebted to Dr. L. Tronstad for much information embodied in this article.

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The Voyage of the *Beagle*, 1831-1836.

ON Dec. 27, 1831, H.M.S. *Beagle*, a ten-gun brig, under the command of Capt. FitzRoy, R.N., sailed from Devonport. "The object of the expedition was to complete the survey of Patagonia and Tierra del Fuego, commenced under Capt. King in 1826 to 1830—to survey the shores of Chile, Peru, and of some islands in the Pacific—and to carry a chain of chronometrical measurements round the world." It is well known how FitzRoy proposed to the Hydrographer that "some well-educated and scientific person" should be invited to join the expedition, how Capt. Beaufort wrote to Prof. Peacock, that he in turn consulted Prof. Henslow, who, as FitzRoy writes, "named Mr. Charles Darwin, grandson of Dr. Darwin the poet, as a young man of promising ability, extremely fond of geology, and indeed of all branches of natural history".

The voyage lasted about three months short of five years. The first land touched was St. Jago, one of the Cape de Verd Islands. In the three weeks spent there, Darwin's observations had two most useful results. They showed him "the superiority of Lyell's manner of treating geology" in the first volume of the "Principles", in spite of

Henslow's well-meant warning "on no account to accept the views therein advocated". It was there, too, that it "first dawned on me that I might perhaps write a book on the geology of the various countries visited, and this made me thrill with delight. That was a memorable hour to me."

From St. Jago the *Beagle* crossed the Atlantic, by way of the St. Paul's Rocks and Fernando Noronha, to Bahia in Brazil. Nearly three and a half years, from March 1832 to July or August 1835, were spent at various ports on the South American coasts from Bahia southwards to the Falkland Islands and Tierra del Fuego, and then up the west coast to Valparaiso and Callao. From the latter port the *Beagle* sailed westwards, with long stops in the Galapagos Islands, Tahiti, New Zealand, and Australia, then by Keeling Island, with its coral reefs, Mauritius, Cape Town, St. Helena and Ascension, and once more to Bahia, returning to England in the autumn of 1836.

During the long pauses at the various South American ports, Darwin made many an excursion inland. From Bahia Blanca he crossed the Pampas and dug out the remains of "great fossil animals covered with armour like that on the