CXL.—*The Passivity of Metals. Part I. The Isolation of the Protective Film.*

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THE alteration in chemical properties conferred on iron and other metals by oxidising treatment has been attributed by some investigators to a protective film of oxide, oxygen-alloy, or other material, and by others to some essential change in the metal itself, or to the removal of a supposed catalyst. Many chemists have hesitated to accept the oxide-film theory chiefly because (1) no film is usually visible, and (2) iron which has been covered with a visible film by heating is often not passive. However, recent work (Evans, *Nature*, 1926, **118**, 51) has shown that electrolytic iron exposed to air or oxygen at different temperatures undergoes absolutely no *visible* change until the oxide film reaches the thickness requisite to give the first yellow interference tint. Thinner films are quite invisible, and yet they give good protection against attack by copper nitrate—better protection, in fact, than thick visible films, which fail locally at points representing pores or cracks, causing deposition of copper on the outer surface of the oxide scale. It is noteworthy that pure iron, rendered active by abrasion, becomes passive when exposed for a few hours to dry air at the ordinary temperature.

It seems at least possible that the production of passivity upon iron by immersion in solutions of oxidising agents, or by anodic treatment in an alkaline liquid, may be due to films too thin to give interference colours. Indeed, it is clear that the greater the specific protective character of the material composing the film the less likely is the thickness to reach the visible range, since the film will hinder its own growth by excluding the oxidising agent from the metal below; only when the protective character of the material is imperfect is a visible film to be expected. This is found to be the case. Ordinary anodic treatment in sodium hydroxide solution renders iron passive, but produces no visible change; if an alternating current is superimposed on the direct current, however, attack upon the iron occurs, and colours (straw-yellow, gold, reddish-brown, and purple) appear in turn on the iron (Allmand and Barklie, *Trans. Faraday Soc.*, 1926, **22**, 34). Likewise, immersion of iron in pure potassium chromate solution causes no corrosion and produces no marked change in appearance; but if a chloride is present in the chromate solution, corrosion occurs locally, and around the points of attack bright colours (yellow, red-mauve, and blue) may be seen, similar to those obtained by heating iron in air at high temperatures (Evans, *J. Soc. Chem. Ind.*, 1925, **44**, 163T). Again, specimens of zinc partly immersed in sodium chloride solution develop colours over a zone near the water line; after drying in air, this zone is found to be blackened by copper sulphate solution more quickly than the parts of the zinc displaying no visible film (Evans, *Ind. Eng. Chem.*, 1925, **17**, 366).

In such cases, the very fact that the film has become thick enough to give colours is a sign that it is imperfectly protective. An efficient protective film will nearly always be invisible as long as it is in optical contact with highly reflecting metal. It is true that sometimes a considerable deposit can be seen on metal which has been rendered passive, but the incoherent appearance of such deposits is sufficient to show that they are not protective films, although their presence is evidence that the liquid is saturated with some compound—a condition favourable for the production of a true film. The arrival and departure of such deposits do not always correspond to the arrival and departure of passivity (compare Müller, *Z. Elektrochem.*, 1924, **30**, 401; Hedges, J., 1926, 2878).

The rational method of rendering visible a film too thin to give interference tints is to separate it from the metallic basis by dissolving away the latter from underneath; films of such thicknesses are readily visible if backed by air or a medium such as water, which has no great reflectivity. Various early attempts by the author to isolate in this way a film from passive iron were unsuccessful, probably owing to the presence of a second phase (*e.g.*, cementite, Fe_3C) which could not easily be dissolved away with the metal. Through the kindness of Dr. W. H. Hatfield, who has provided a considerable quantity of electrolytic iron, this obstacle now has been removed. The material had been fused in a vacuum in a magnesia crucible before being rolled into sheets 0·12 mm. thick. Analysis showed C, 0·04; Mn, 0·025; Si, 0·010; S, 0·013; P, 0·017; Ni, 0·09%. The main impurity (nickel) would certainly be present in solid solution, and could therefore be considered harmless. Photomicrographs of the material showed a satisfactory absence of inclusions.

Before each experiment, except where otherwise stated, the iron was ground with washed emery flour, applied on unbleached linen, which had previously been boiled out with water; it was then rubbed with filter paper. In special cases, emery paper, in seven grades of coarseness, was employed, whilst in one series of experiments a carborundum disc was used to abrade the surface.

Anodic Method of removing Transparent Skin from Passive Iron.—Specimens of iron rendered passive by immersion in a solution of potassium chromate, potassium nitrite, or sodium hydroxide, or by exposure to dry air, were subjected to anodic treatment, so as to dissolve away the metallic iron from the interior and leave the skin. This result could be obtained under a fairly wide range of conditions. In a typical experiment, a strip of iron 0·5 cm. wide was immersed in *M*/20-potassium chromate solution for 2½ hours at 22°, and was then washed and dried; the bottom of the strip was trimmed off, and the specimen was then clamped vertically in *N*/10-sodium chloride solution, so that only the lowest 1 cm. was actually immersed, and subjected to anodic treatment with a current of 6 milliamps.; precautions were taken that the cathodically-produced alkali did not come near the anode. Dissolution of the metal started at the bottom, and worked upwards; the action did not cease at the water level, for after about 16 hours the metal just above the water line was quite transparent, the whole specimen retaining essentially its original shape; however, when the transparent zone had spread upwards a few mm. above the water level, the lower portion usually broke off just above the water level, thus stopping the flow of current. Similar results were obtained with iron rendered passive by the other methods mentioned above.

After each experiment, an examination under a binocular microscope was carried out. The envelope of the electrode after anodic treatment consisted of two thin transparent parallel membranes united at the two edges. Between them was enclosed an appreciable quantity of liquid rich in ferrous chloride; a little residual metallic iron was found within the envelope in many specimens, but by far the greater part of the metal had in every case been dissolved away. The enveloping membrane consisted of ferric oxide and, probably owing to its thinness, was only pale yellowish-grey by transmitted light when freed from adhering material; but in nearly every case there was attached to it a quantity of " rusty " ferric hydroxide having a distinct yellowish-brown colour. On the immersed portion, this rusty hydroxide was often observed hanging from the outside in loose tufts, but it also occurred in the interior, where it was unequally distributed in patches clinging rather closely to the inner surfaces of the two membranes. Above the water line there was usually a much smaller amount of the yellowish-brown hydroxide, and for that reason most of the specimens became more completely transparent above the water level than below it. There was also more residual iron in the part below the water line, thus causing local opacity.

There seems but little doubt that the transparent envelope represents a skin present upon the metal before the anodic treatment commenced; the two parallel membranes represent the two surfaces of the original electrode. The envelope preserved in detail the original outline of the specimen; in some cases, the microscope revealed in the transparent skin tiny opaque inclusions arrayed along a series of parallel lines at right angles, unmistakably representing the original grinding directions; these lines are discussed later.

The yellowish " rusty " ferric hydroxide can be regarded as a hydrolysis product of ferric chloride or as an oxidation product of ferrous chloride. A reason for the fact that it occurs more frequently below the water level than above it is suggested by the ordinary principles of probability: above the water line, capillary forces will tend to keep the two parallel membranes close together, and the volume of iron salt solution enclosed between them will be small; below the water line, slight separation of the two skins may occur, and this fact (along with the possible occurrence of soluble iron salts outside the membrane) accounts for the close packing of the " rusty " patches. In only 3 experiments out of 57 was the *immersed* portion of the electrode converted into a transparent pseudomorph free from the rusty type of hydroxide; but in several cases where the central parts of the immersed portion were rendered almost opaque in places with rusty patches, the edges (where the two membranes necessarily approached close together) were seen to be transparent and nearly colourless.

It was remarkable that the transparent envelope was usually strong enough to retain the shape of the original electrode. The bulging referred to above was usually so slight as almost to escape notice; sometimes, however, the two membranes gaped far apart, with considerable distortion of the whole shape. Occasionally there was a tendency to curl up, whilst not infrequently small local rents occurred on one or both skins. Such imperfections were actually rather useful in revealing the fact that without doubt the transparent skeleton consisted of two separate membranes.

Iodine Method of Removing the Skin.—More definite information regarding the function of the skin in protecting iron was obtained by studying the action of iodine on passive iron; a saturated solution in 10% potassium iodide was found convenient. Pieces of iron were rendered passive in potassium chromate, and a deep scratch was made along the middle of each of them. They were then clamped vertically so as to be partly immersed in the iodine solution. After 2 days, the metal had become corroded through completely at numerous points along the line of the scratch, and usually also at points on the water line. Elsewhere there was no serious loss of thickness, except at isolated points mostly situated near the edges. The greater part of the surface, however, was covered with a transparent film which could easily be removed; below the skin, the metal was distinctly corroded, especially close to the scratch. One specimen removed in the early stages had areas over which the skin, although already visible, was still adherent; around the boundaries of these areas, the corrosion below the skin was very slight. This seemed to show that the detachment of the transparent skin was mainly due to the dissolution of the metal below. No evidence was obtained for the conversion of the metal itself to an inert form as suggested by Russell (*Nature*, 1925, **115**, 455; 1926, **117**, 47). The relative immunity of the unscratched places appears undoubtedly to be due to the fact that the skin obstructs the flow of iodine to them; it may be that a slow passage of iodine can occur through the film itself, but the attack takes place far more rapidly where the film has been removed, loosened, or undermined, or where cracks exist in it.

Pieces of freshly abraded iron clamped vertically in the iodine solution behaved quite differently, being corroded away completely up to the water line within a day; just above the water line, there remained a transparent zone consisting of a double membrane, evidently caused by the iodine solution rising by capillarity and corroding the metal between the two oxide skins produced by the action of the air.

The transparent skin freshly removed from passive iron after iodine treatment consisted of flakes of appreciable size, curling rolls 2 to 3 mm. long being quite common; these always broke up into microscopic fragments when washed. The flake-fragments were washed repeatedly by decantation until soluble iron salts were removed, and then examined under the binocular microscope. More than 100 different preparations of flakes, derived from iron rendered passive under different conditions, were studied, but the following features were characteristic of practically all.

The flakes consisted of non-magnetic ferric oxide, and were quite transparent; they often showed a tendency to curl into rolls. Each flake when viewed by transmitted light was seen to be covered with a series of dark lines, the nature of which depended on the preliminary abrasion of the iron. If the iron had been ground in one direction only, there was a single series of parallel dark lines on the flakes; if it had been ground in two directions, the flakes displayed two sets of dark lines intersecting at a corresponding angle. When the flakes were viewed by reflected light at a suitable angle, the dark lines were found suddenly to become bright lines, and there is no doubt that they represent the crenulations left on the surface of the iron by abrasion. Thus the film actually represents the oxidised surface of the original specimen of metal. In most preparations, series of opaque particles were also visible, arranged in rows parallel to the dark lines; these were partly residual iron and partly included grains of abrasive. The film showed a marked tendency to break up along lines parallel to the grinding directions, so that the film obtained from iron ground in two directions at right angles tended to produce roughly square or rectangular flake-fragments.

Although the flakes just described represent, beyond all doubt, the original oxidised surface of the metal, they usually carried a certain amount of secondary ferric hydroxide (doubtless due to hydrolysis of ferric iodide) which could be removed by washing with $N/10$-hydrochloric acid. Experiments performed under the microscope with acid containing thiocyanate showed that most of the dissolution of the adherent hydroxide occurred within 2 minutes, but the flakes themselves remained unchanged even after many hours. Special experiments showed that the flakes were rendered only very slightly thinner after being washed with acid for 3 hours, apart from the removal of hydroxide. However, the flakes which, before washing, appeared rusty yellow to the naked eye, became, after acid-washing, almost white when viewed suspended in water; when examined under the microscope, they still had a very pale, slightly yellowish-grey colour by transmitted light. The existence of the striæ on the flakes makes it easy to distinguish them from any fragments of that membranous ferric hydroxide film which sometimes forms on the air–water interface of ferric salt solutions, as the result of hydrolysis. This membranous hydroxide sometimes reaches "interference-colour thickness," and is entirely different in appearance and properties from the striated films; a long study of the latter made it absolutely certain that these could not be the result of hydrolysis. To avoid any possible mistake, most of the flake preparations mentioned above were obtained by using stoppered vessels entirely filled with iodine solution, thus avoiding the formation of membranous hydroxide altogether. Each preparation was divided into two portions, one only being washed with acid; each portion was examined separately.

Some further information regarding the distribution of iron in the flakes was obtained by treating them with 8% hydrochloric acid containing either ferrocyanide or ferricyanide. The former reagent conferred a beautiful blue tint on the flakes, which nevertheless retained their form for some hours; the dark lines representing the emery grooves became a deeper blue than the rest. This "blueing" treatment was found useful for showing up flakes which were so thin as to cause no appreciable absorption of light. Such flakes had been recognised previously only by the fact that they carried the usual series of dark parallel lines or opaque specks which could be clearly seen, although the material of the flake itself was invisible; the application of the "blueing" method, however, rendered visible the flakes as a whole. Ferricyanide was useful in showing up the particles of residual metallic iron, which produced a deep expanding circle of blue before the main part of the flakes showed any colour at all. Thiocyanate treatment also gave interesting information, but owing to the solubility of ferric thiocyanate a special method of application was necessary. A number of flakes, suspended in a water-drop, were placed on a glass slide under the microscope; the water was sucked away with tiny pointed strips of filter-paper, leaving the flake on apparently dry glass. Actually, of course, the glass was covered with an invisible film of moisture; consequently, on placing drops of acidified thiocyanate on the glass *near*, but not in contact with, the flakes, these assumed a pink colour within a few seconds, owing to diffusion of the salt through the moisture film.

Films Produced by Exposure to Air.—Strips of electrolytic iron freshly abraded with emery-paper were held at one end and heated red-hot at the other, so as to produce a temperature gradient. This left the iron without visible change at the cold end, but in the centre the three orders of interference tints appeared, whilst at the hot end there was a region covered with comparatively thick scale. The strip was then cooled and quickly cut into sections, which were separately treated with iodine to isolate the oxide film from each. The film peeled off in big flakes which were largest where the film was thickest. These were washed with water (portions of each also with acid) and examined microscopically.

The main portion of the oxide skin, both on the " apparently unchanged " and " interference-colour " regions, consisted of transparent, non-magnetic ferric oxide, similar to that obtained from passive iron. Opaque magnetic scale began to appear as a separate layer below the transparent films about the region of second-order colours, and became very thick at the red-hot end. Confining attention to the ferric oxide film, no sharp transition of properties was noticed on passing from the " unchanged " region to the " interference-colour " region. Apart from a gradual increase of thickness and strength of the films as one passed along the strip, the same characteristics were seen throughout. All the films showed striæ representing the original emery grinding, and in the thicker films the corrugated character of the flakes was conspicuous at the edges. Moreover, except for the very thin film at the cold end, there was a well-marked tendency to break along the directions of abrasion; the very thin flakes from the cold end were much more ragged and tended to shrivel, or to cling together in flocks, making observation difficult.

Ferric oxide films are by no means so transparent as the lead oxide films separated from heat-tinted lead (Evans, *Proc. Roy. Soc.*, 1925, *A*, **107**, 231), and the light-absorption produced by the thicker films was considerable. The flakes from the second- and third-order regions, although translucent, were dark brownish-grey by transmitted light. With the thinner films, the amount of light transmitted increased; the first-order flakes were brownish- or yellowish-grey, the tint being only very slightly modified by interference (the optical principles involved will be discussed elsewhere). With the films obtained from the " unchanged " region, the light-absorption diminished still further, but the flakes retained a slight yellowish-grey tinge which was still discernible at a thickness of one-quarter of that of the first " straw-yellow " film. By matching the absorption of two different flakes with points on a wedge-form light-filter, the approximate ratio of the thicknesses could be determined. For instance, it was found that when the iron had been abraded with emery paper of " 1½ grade " (Oakey), the maximum protection of the metal against the action of either copper nitrate or iodine solution was afforded with a film of thickness about 80—90% of that of the " straw-yellow tinted " metal.* Films having a smaller or greater thickness gave less protection against both reagents. The zone of fairly great resistance to iodine extended into the yellow region, but fell off rapidly in the mauve-red, whilst the iron showing the first-order blue was eaten away almost completely in a period which caused very little corrosion of the yellow-tinted metal. Such information, however, has no general significance. As will be explained below, by the use of finer grinding materials, good protection is obtained at thicknesses far below those just quoted; indeed it is not impossible that a continuous unimolecular film extending over stress-free iron would give protection (compare Vernon's results on copper, J., 1926, 2273).

The most surprising result is that the thicknesses of different flakes taken from the same area of the specimen show a considerable variation. This becomes particularly marked in the case of the films responsible for the first-order blue and subsequent tints, and a microscopic study of these has suggested the cause. Such films when freshly removed showed numerous holes, and beside these holes, or covering them, were smaller pieces of film usually attached as " flaps " to the main films. Evidently, then, these thick films have a marked tendency to crack, as suggested by earlier work (*Nature*, 1926, **118**, 51); at each crack oxygen would gain access to the exposed metal and produce a second film below. If after the iodine treatment this second film remains adherent to the first, a local thickening will be visible at the site of the crack; if it does

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* The *actual* thicknesses of the " heat-tint " films have long been the subject of discussion. If we adopt the value 2·36 for the refractive index of ferric oxide towards blue light (Kundt, *Wied. Ann.*, 1888, **34**, 484), and if we neglect the error due to the difference between the phase-changes connected with the reflexions at the two interfaces (see Evans, *J. Soc. Chem. Ind.*, 1926, **45**, 211), then the thickness of the first straw-yellow film should be about 400 Å. The thickness cannot be expressed directly in terms of layers of molecules, as this will depend on the crystal-orientation; but it may be stated that *X*-ray studies by Davey (*Physical Rev.*, 1923, **21**, 716) have shown that the side of the equilateral triangle formed by the three oxygen atoms of the Fe_2O_3 molecule is 5·035 Å.

not adhere, a separate specimen of the second film will be obtained, which will in general be thinner than the average thickness proper to the tint under consideration. Evidence of similar thickening around sites of cracks was obtained for films too thin to produce interference tints on some specimens abraded with the carborundum disc; the cracks followed the grinding directions. In general, however, the films freshly separated from the " unchanged " region did not show cracks or holes as long as they were suspended in water, although holes developed when they were dried. The very thin flakes, which have a ragged—as opposed to a square—outline, probably represent fragments of a discontinuous film which did not completely cover the surface of the metal. It is easy to understand why the continuous films of intermediate thickness give better protection than films of greater or smaller thickness.

We have now to consider the cause of the cracks in the thicker films, and of the discontinuity in the thinner films. The cracking in the *thick* film is undoubtedly due to the compressional stresses resulting from the fact that iron oxide occupies a larger volume than the iron required to produce it (compare Pilling and Bedworth, *J. Inst. Metals*, 1923, **29**, 529). The " saucer-shaped " form of scale-fragments sometimes thrown off from heated metals, especially copper, is a visible proof of this compression. Mechanical considerations show that this cracking will occur more readily with thick films than with thin.

The discontinuity of films of thickness *below* that needed to produce maximum air-passivity seems to be due to quite different causes. At first, it might be thought that it is the consequence of a limited velocity of oxidation, but experiments on film formation in air at the ordinary temperature do not support this view. Several specimens of iron were quickly ground with the carborundum disc, held in air for a definite time, and plunged into iodine. Blank experiments were made with specimens ground under the surface of iodine; these produced no flakes, except for a very small quantity which probably came from the edges of the specimens—places difficult to grind satisfactorily under these conditions. But exposure to air even for so short a time as 8 secs. produced a large crop of flakes which, although ragged and shrivelled, must have occupied a considerable fraction of the whole surface. Exposure to air for longer periods (11, 22, 43, 165 secs.; 5, 10, 20 mins.) gave flakes which became less ragged as the exposure increased. It would appear that the surface oxidation of iron at low temperatures is quite rapid, and the non-protective character of the films in the early stages is due to some other cause.

A further series of experiments showed that the time required to produce effective air-passivity to copper nitrate solution increased with the coarseness of the abrasive used to prepare the surface. Strips of iron were ground with emery paper of six different grades, and at definite intervals drops of $M/20$-copper nitrate solution were placed on them. The finest-ground strip became unaffected by the copper salt within a few minutes; that ground with the coarsest paper required some hours. No definite "periods of passivation" can be stated, since, during the transition from the active to the passive state, copper-deposition becomes confined to a limited number of points (evidently gaps in the film), and these points gradually become more and more sparsely distributed as the time goes on. During the transition period, therefore, some of the drops on a strip will show copper deposition and others none; a similar lack of reproducibility has been noticed by McCulloch (*Trans. Amer. Electrochem. Soc.*, 1926, **50**, 197), who has found that large pieces of "passive" iron are more liable to fail than small pieces, no doubt because there is a greater probability of a discontinuity occurring somewhere in the film when a large portion is being tested.

The important effect of the abrasive on the time needed for passivity suggests that the cause of local failure of the films produced by air in the early stages of oxidation is due to the internal stresses left by the grinding. A cold-worked metal is necessarily subjected, in different parts, to tensile and compressional stresses; normally the tensile stresses are in equilibrium with the compressional stresses, but if the outer surface undergoes removal or chemical alteration, this equilibrium is destroyed, as shown by Heyn (*J. Inst. Metals*, 1914, **12**, 3) and by Hatfield and Thirkell (*ibid.*, 1919, **22**, 67). When, therefore, the surface layers of cold-ground iron become converted into oxide, forces will at once become available to produce cracking in the films first formed, and although fresh oxidation will keep "repairing" the cracks, cracking will continue until the internal stresses are sufficiently diminished. This will occur quickly if the iron has been ground with fine abrasive, but will require a long time if it has been ground with coarse abrasive, thus explaining completely the observed facts.

It seems possible that the thickening of the film with time may be due rather to the passage of oxygen through the continually opening cracks than to diffusion through the substance of the film itself, diffusion through a solid being a slow process at the ordinary temperature; this would provide an explanation of the variation of the film thickness from place to place. If this explanation is correct, we may expect to find that coarse-ground iron develops films of a greater thickness than fine-ground iron. An actual study of the films from iron ground with six grades of emery confirms this expectation in a noteworthy manner, the films coming from the iron ground with the finest emery having at the most only one-quarter of the thickness of those derived from iron ground with the coarsest emery, and probably very much less. Measurement of the thinnest films is very difficult, as they contain much opaque residual iron, and the film (which seems almost incapable of existing without support) tends to shrivel around the places where this stronger supporting material is present.

When drops of $M/20$-copper nitrate are placed on specimens of iron which have previously been exposed to air for sufficient time to acquire passivity, no copper is deposited, but a sequence of interference tints slowly appears, indicating a film-thickening. This is another example of the general principle that agencies which tend to cause a film to break down may, under less favourable conditions, simply cause it to thicken. The sequence of colours indicates that the film reaches its greatest thickness at the drop-edges (the usual seat of a breakdown), and becomes continually thinner as the centre of the drop is approached; this is confirmed by converting the film, which consists of ferric oxide, *in situ* into Prussian-blue. A greater final thickness is reached, *ceteris paribus*, on coarse-ground iron than on fine-ground iron, no doubt because the initial thickness is greater when a coarse abrasive has been used.

Films produced by Potassium Chromate.—When electrolytic iron is ground in air and then placed in a solution of potassium chromate, there will usually be the beginnings of an oxide film on the metal before immersion, as a result of oxidation during grinding. As a rule, however, the metal will not be passive towards copper nitrate when it enters the solution, but it gradually acquires passivity through the action of the chromate.

Pieces of electrolytic iron were ground with emery, and at once placed in potassium chromate solution in a thermostat for definite times. The films were then removed with iodine, and studied. A " blank " was performed with metal which had been ground in air like the others, but not immersed in chromate. The flakes from the " blank " (due simply to air exposure during grinding at a temperature unavoidably raised slightly through friction) were of the ragged, shrivelling type characteristic of a discontinuous film, but gradual lengthening of the chromate treatment rendered the flakes less ragged and squarer. The aspect of the metal left after the flakes had been removed by iodine also suggested that the film became more nearly continuous with the immersion in chromate. In the blank, the metal was completely corroded away by the iodine over a large area, but as the chromate exposure was increased the area suffering perforation gradually lessened.

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 air, but in addition there is some evidence that the chromate causes thickening of the film. Preparations of flakes were obtained from iron which had been ground with fine emery flour and immersed in *M*-potassium chromate for 4, 8, 16, 32, 128, and 256 mins., respectively, at 11·4°, and the thickness of the flakes was measured; a similar study was made of flakes separated from iron ground with coarse emery. The films obtained from every specimen showed the usual variation of thickness, the thickest flakes being generally 1½—2 times as thick as the thinnest. But there seemed little doubt that the average thickness of "typical" flakes increased somewhat with the time of exposure to chromate solution; the thickening, however, became too slow to be followed when the thickness of typical flakes reached a value about 85—90% of that obtained from iron heat-tinted to the commencement of the first-order yellow; at this stage, the film still contained thinner places (70% of the thickness of the incipient yellow) whilst individual flakes already showed a thickness which, if continuous over the whole surface, would have produced a visible yellow colour. It is not surprising, therefore, that a prolonged exposure to chromate solution can actually confer a yellow tint. Two years ago, the author (*J. Soc. Chem. Ind.*, 1925, **44**, 163T) showed that samples of commercial iron placed in potassium chromate solution for 3 weeks acquired a slight, permanent, yellow tint, whilst similar specimens placed in chromate–chloride mixtures developed yellow, mauve-red, and blue patches around the points of breakdown; the colour sequence indicated a gradual thickening of the film as the site of corrosion was approached, a phenomenon exactly analogous to the variation of thickness recognised at a lower range in the present research. Exposure to air for similar periods did not cause tinting.

Attention must be directed to one difference in the behaviour of continuous and discontinuous films. When a piece of iron, rendered passive by long immersion in potassium chromate solution, is placed in iodine for a sufficient time to loosen the skin, the specimen can be withdrawn with the film still clinging to the metal, although a layer of liquid is present between the film and metal. On gently agitating the specimen with clean water, the film comes off in quite large flakes. If, however, a freshly ground piece of iron is placed in iodine, no film is found on the metal when it is withdrawn, for any rudiments of a film produced by air-treatment during grinding have already passed away into the iodine solution, whence they can afterwards be recovered by the usual settling process.

Electrolytic iron is rendered passive by dry air as readily as by potassium chromate solution. Thus, two specimens of electrolytic iron were treated, one in dry air and the other in *M*-potassium chromate solution, for 22 hours; they were then both quite passive towards *M*/20-copper nitrate and remained quite unaffected in that solution for 13 days; even after 8 weeks, they were both bright and free from copper, although there was a little flocculating rust at the bottom of the vessels. Steel (C, 0·18; Mn, 0·56; Si, 0·04; S, 0·047; P, 0·028; Ni, 0·10%) behaved differently, however: a sample exposed as above to air broke down in *M*/20-copper nitrate within 4 minutes, copper being deposited freely; a sample treated in chromate survived for 20 minutes. Here one must consider the effect of couples set up between the iron (as anode) and cementite (as cathode); electrochemical action of the chromate will necessarily tend to build an oxide film over the anodic area, which must continue until the whole surface becomes equipotential and current ceases to flow; in that condition, the surface is likely to be equipotential in copper nitrate also. There is no *a priori* reason to suppose that exposure to dry air should bring about a surface which would be equipotential in copper nitrate solution. Hence the advantage of obtaining passivity with an electrolyte, such as potassium chromate, is obvious.

Effect of Chlorides on Passive Iron.—The well-known action of chlorides in dispelling passivity is capable of two different explanations: (1) Mere immersion in chlorides may be supposed to loosen or peptise the film, quite independently of the passage of electric current; (2) when passive iron is made an anode, the discharged chlorine ions may be capable of passing through the protective skin, producing corrosion of the metal below and so rendering the skin loose and non-protective. If the first explanation is correct, mere immersion in a chloride solution—under conditions which would preclude the existence of an *E.M.F.* between different parts of the metal—should render passive iron active; if the second explanation is right, the iron should remain passive.

Several experiments were performed to test this point. Discs of electrolytic iron were "whirled" in *M*/20-potassium chromate solution for periods of 30—60 min., thoroughly washed, and then "whirled" for a similar period in sodium chloride solutions (*N*, *N*/10, and *N*/20, in different experiments); for this purpose, the "eccentric whirler," designed to minimise the *E.M.F.*'s due to differential aëration, was employed (Evans, "Corrosion of Metals," 1926, p. 108). After whirling, the discs were taken out, washed, and dried. Spots of rust, apparently marking the site of pores relatively inaccessible to dissolved oxygen, were present on some discs, but in all cases there were large areas still bright and unchanged; many specimens—apparently those most free from pores—were practically free from rust spots. When drops of *M*/20-copper nitrate solution were applied to the rust-free areas, the metal was found in every case still to be passive, suggesting that the first explanation is wrong. Other experiments at 95° also pointed to the fact that mere immersion in a chloride solution without the passage of current does not dispel passivity. On the other hand, under conditions where the anodic discharge of chlorine ions is possible, chlorides render the iron capable of attack. Iron discs, after the whirling in potassium chromate, suffered rapid attack when made the anode in *N*/10-sodium chloride solution, an *E.M.F.* being applied from an external cell. Again, they were blackened within a minute by contact with *M*/20-copper chloride solution, the replacement of iron by copper being in effect equivalent to anodic attack; they also suffered rusting when drops of *N*/10-sodium chloride were placed on the surface, the *E.M.F.* in the latter case being attributable to differential aëration. These facts indicate that the second explanation represents the more important cause of the activating influence of chlorides.

A study of the anodic attack of previously passive iron in a chloride solution supports this view. Specimens of iron which had been ground with FF emery paper were whirled in *M*/20-potassium chromate, then washed, dried, and subjected (without trimming of the edges) to anodic treatment in *N*/10-sodium chloride solution. At numerous points, dark spots appeared, situated mainly at the parts least accessible to oxygen; they were, for instance, arranged along the grooves left by the grinding and were clustered more closely near the bottom of the electrode than near the water line; along the water line itself, however, there was a row of closely-arranged spots (rather smaller than the others), and grey patches also extended along the edges of the electrode. The whole appearance suggested that at certain points chlorine ions had pierced the skin, producing corrosion below it, and that the skin had been undermined and loosened around these points, the areas thus affected gradually spreading outwards until they met one another. Steel containing chromium, which shows efficient "air-passivity," behaved in an analogous manner. A "stainless steel" knife-blade anodically treated in *N*/20-potassium chloride solution was corroded away entirely around the edges. In the centre, corrosion occurred in circular spots; at many of these spots the blade became completely perforated, with marked undercutting of the surface of the surrounding steel, although between the spots in question the surface remained quite uncorroded.

One question still remains unanswered: Do the chlorine ions themselves perforate the skin, or do they pass through holes which already exist in the skin but which are impervious to other ions? By reason of size alone, chlorine ions might be expected to pass through pores impermeable to polyatomic ions, although our knowledge of osmotic phenomena shows that size is by no means the only factor which influences selective permeability. There is at present no convincing evidence of penetration through pre-existing pores, but the author is disposed to believe that such pores do play a considerable part in the breakdown.

Water-line Attack on Passive Metal.—Many earlier investigators have noted that a passive anode often suffers a slow dissolution, although only a small fraction of the current passing is concerned in corrosion, the remainder being devoted to the production of oxygen. In the present experiments, it was observed that this slow dissolution is mainly due to attack along the water line. A strip of electrolytic iron, 0·8 mm. broad, was subjected to anodic treatment in *N*-potassium sulphate; the cathode was a large iron plate, and the two electrodes were joined to a 6-volt accumulator before immersion in the liquid. The anode was introduced to a depth of only 3 mm., producing instantaneously a high local current density, so as to cause immediate passivity. A vigorous evolution of oxygen was observed over the immersed surface; along the water line, however, the metal was quickly eaten away, leading to perforation; after 37 mins., complete severance occurred at this level, and the lower part of the electrode—still almost uncorroded—fell to the bottom of the vessel. Several other experiments gave similar results.

With air-passive materials, anodic attack at the water line was sometimes very marked. A plate of "staybrite" steel (containing Cr, 18; Ni, 8%) was made the anode in *N*/10-sodium chloride at an average *C.D.* of about 50 milliamps./cm.^{2}. At first, it appeared to act as an inert electrode, oxygen being freely evolved, with a little chlorine. After 15 mins., however, the solution was seen to be turning yellow, and black points appeared at the water level, gradually extending to form a continuous black line. After 18 hours, the immersed portion was still practically uncorroded, but along the water level the corrosion had burrowed deep into the metal, with marked undercutting of the resistant surface layers.

Water-line attack is a marked characteristic of the passive state. The application of an external *E.M.F.* is unnecessary, for it can be produced by simple immersion in iodine solution. Previous work (*J. Soc. Chem. Ind.*, 1925, **44**, 163T) had shown that iron immersed in a chromate–chloride solution suffers intense attack along the water level, although in a chloride solution free from chromate the zone close to the water line is much *less* attacked than the part lower down; in the case of an air-passive material, the attack by a chloride solution occurs at the water line even in the absence of chromates (Stowell, Congress of Chemists, 1926). The suggestion made in previous papers—that the protective film tends at the water line to cling to the gas–liquid instead of the metal–liquid interface, thus initiating a breakdown—explains all the phenomena observed in the present research. It is not claimed that all cases of water-line corrosion are produced in this way; no doubt there are different causes for the special attack upon this region (Hedges, J., 1926, 831; Evans, *J. Soc. Chem. Ind.*, 1924, **43**, 127T; 1925, **44**, 163T; J., 1925, **127**, 2484). Indeed the term "water-line corrosion" has been used to cover many distinct phenomena, some of which do not occur strictly at the water level itself, but just above or just below it.

Action of Nitric Acid on Electrolytic Iron.—Although diluted nitric acid (*e.g.*, *d* 1·2) acts rapidly on electrolytic iron, the concentrated acid (*d* 1·4) was found to have little action. The liquid became yellow along the metal surface, and a few bubbles of gas were produced, but after about 2 mins. all reaction ceased, and the metal could be kept totally immersed in the acid for hours without change. If the acid was then poured off and the specimen quickly washed, the metal was usually found to be passive towards *M*/20-copper nitrate solution, although occasionally a specimen became covered with copper rapidly, indicating that the passivity produced by nitric acid may break down spontaneously. The specimens showed no resistance to iodine solution.

When pieces of electrolytic iron were dipped below acid of *d* 1·4, then taken out and allowed to drain, after some seconds a violent reaction would start quite suddenly at some point (usually at the top of the wetted area), and travel downwards rapidly until the whole area was evolving bubbles. Soon the reaction would die away, since the acid adhering to the strip became exhausted, and if the strip was then dipped again in acid, and moved about, the brown corrosion-product quickly dissolved away, revealing the bright metallic surface, which appeared quiescent. The spontaneous breakdown of the passivity on removing the metal from the liquid is easily understood, since drainage must soon bring the air–liquid interface close to the metal–liquid interface. The rapid transmission of the reaction downwards from the point of breakdown is perhaps partly due to an undermining of a protective film, but is probably largely connected with the fact that one of the products of the action, *viz.*, water, is known to stimulate the attack. Any reaction in which gaseous oxides of nitrogen are expelled must increase the ratio $H_2O : N_2O_5$ in the residual liquid, and thus will increase the velocity of the change. Perhaps the rise of temperature, and the passage of electric currents between the active and the passive regions as suggested by Heathcote (*J. Soc. Chem. Ind.*, 1907, **26**, 899) and Lillie (*J. Gen. Physiol.*, 1920, **5**, 107, 129), may also aid the transmission. Numerous observations support the view that one of the corrosion products is, in effect, a catalyst. When a strip wetted with nitric acid was allowed to drain until reaction had just started at a point, and was then plunged into nitric acid with sufficient motion to dissipate the corrosion products in the acid, the transmission ceased and the whole became quiescent; if, on the other hand, the reacting strip was introduced gently into the acid, so that corrosion products could accumulate, the reaction became violent at the water level, causing the strip to be eaten right through, and the lower part, which was usually quiescent, would fall to the bottom of the vessel within a minute. Heathcote's observation, that activity spreads downwards more easily than it spreads upwards, also receives an explanation if we assume that the heavy mixture of corrosion products contains a catalyst.

Of the other products of reaction, nitric oxide, nitrogen peroxide, nitrous acid, and ferric nitrate do not appear to have any marked effect in initiating attack. Nitric acid (*d* 1·4), to which either solid potassium nitrite or ferric nitrate has been added, does not act on electrolytic iron introduced into it. Indeed, ferric nitrate, the final reaction product, has been stated by Ramann (*Ber.*, 1881, **14**, 1430) to favour passivity, and this may be the explanation of the fact that intermediate concentrations of nitric acid can produce either corrosion or passivity according to the procedure employed. For instance, nitric acid (*d* 1·32) caused rapid evolution of gases when an iron strip was introduced into it, but if the strip was at once taken out of the acid and, after the evolution of gas had ceased, was then replaced, the whole remained quiescent, the ferric nitrate having produced passivity. Premature replacement of the strip while still reacting led to rapid attack, causing complete severance at the water level.

The ineffective character of the passivity produced by nitric acid renders the investigation of the protective film by the iodine method difficult, but the general analogy between the passivity produced by this and other methods suggests that nitric acid gives rise to a film which tends to break down spontaneously. It is often stated that no oxide of iron exists possessing the requisite properties. Heathcote's work on the rate of dissolution of *powdered* iron oxides by nitric acid rather supports that view. It seemed, however, advisable to perform experiments on the oxide as a *film*, rather than as a powder. Accordingly, strips of electrolytic iron were heated at one end so as to give the usual zones of interference colours due to oxide films, the unheated end remaining untinted. When they were placed in nitric acid (*d* 1·4) no change was observed in the colours even after 3½ hours at 23°; had the acid possessed a rapid solvent action on the oxide responsible for the colours, the tints would have disappeared, or at least altered, in the manner produced in a few seconds by cathodic treatment in dilute hydrochloric acid (compare Evans, *Proc. Roy. Soc.*, 1925, *A*, **107**, 228). When the experiment was repeated with acid of *d* 1·2, the iron was violently attacked at the untinted end; after this end had been completely eaten away, the acid commenced to corrode the iron below the film at the tinted end, causing it to peel off in ragged, microscopic flakes, similar to those produced by the iodine method; the flakes remained undissolved after all the metal had disappeared. A similar peeling could be produced by concentrated acid when 6 days were allowed; in this case, there was practically no formation of bubbles, and the film was obtained in relatively large, transparent flakes. Evidently it is untrue to say that no oxide of iron is capable of resisting the acid to the required extent.

There are many indications that the action of nitric acid is actually capable of producing a film on the metal. In many of the experiments on the action of diluted nitric acid on iron, it was noticed that where the red fumes produced in the reaction swept up over the surface of the iron above the water level, the usual sequence of tints (yellow, reddish-mauve, blue, etc.) was produced, indicating the presence of a film. The very fact that the film had reached visible thickness showed that the physical character was unsuitable to give protection, and it was not surprising to find that in every case the tinted area was not passive towards copper nitrate. But it seems reasonable to suppose that under slightly different conditions the film would be more continuous and would afford better protection, whilst not reaching the thickness sufficient to produce tints; such conditions probably exist in concentrated nitric acid.

The view has sometimes been expressed that the resistance of commercial iron to nitric acid may be due partly to a film of silica, and it was anticipated that iron with a moderate content of silicon would be rendered passive with especial ease. Experiments on several types of the silicon–iron used in electrical machinery showed, however, that the alloys were not specially resistant to nitric acid; one alloy with 3·5% silicon was completely dissolved by nitric acid (*d* 1·40) under conditions which produced a quiescent state on pure iron. These silicon alloys were kindly provided by the General Electric Company.

Examination of Other Metals.—Aluminium, which had been exposed for 6½ hours to air in a desiccator after grinding, on anodic treatment in *N*/10-sodium chloride left a skeleton containing much opaque residual metal, but also a transparent film, the structure bearing signs of the original grinding; the transparent skin was entirely different from the precipitated hydroxide formed in a different part of the cell (where the cathodic sodium hydroxide met the anodic aluminium chloride) and was clearly residual. The iodine method gave confirmation of these results. Aluminium, when freshly abraded or rendered active by immersion in *N*-sodium hydroxide, was quickly attacked by iodine; after 70 minutes' immersion in *M*/20-potassium chromate, it reacted only very slowly. Undermining of the surface layers gave transparent flakes of oxide containing opaque areas due to residual metal. It should be mentioned that the normally invisible skin present on aluminium which has been heated at 800° had already been isolated by Seligman and Williams (*J. Inst. Metals*, 1920, **23**, 169), whilst Bengough and Sutton (private communication) have lately obtained a transparent scale from aluminium previously subjected to anodic treatment in chromic acid.

Copper, when immersed in a chromate solution, becomes covered with a film thick enough to cause a visible browning; it is not surprising to find that this film causes only a temporary protection against silver nitrate. Strips of copper which had been immersed in *M*/20-potassium chromate solution yielded on anodic treatment a skeleton containing some flakes of transparent cupric oxide, bluish-grey by reflected light, some of which bore traces of the original emery treatment, or were continuous with the surface of flakes of residual metallic copper which themselves bore marks of the grinding. There was evidence that the transparent oxide film lacked mechanical strength, and the whole observation was made difficult by the presence of a very large amount of opaque cuprous oxide, bright red by reflected light—evidently a secondary product.

Russell's electronic view of passivity (*Nature*, 1925, **115**, 455; 1926, **117**, 47) is based largely on the assumption that the phenomenon is confined to a small number of metals possessing certain common features in their sub-atomic structure; undoubtedly the metals which are believed to have the sub-atomic structure in question include those which are easily obtained at will either in the active or in the passive state. There seems, however, no reason to draw a line between such metals and those in which one state is far more stable than the other. On considering the "long" form of the Periodic Table, we see on the extreme left the alkali metals, which, having highly soluble oxides, are unlikely normally to show passivity. To the right of these we find typical " A group " metals, such as aluminium and tantalum, which for some purposes can be regarded as being almost permanently passive; the oxide film causes remarkable permanence in air in spite of the negative electrode potential. To the right of these again are metals such as iron and nickel, in which both active and passive states are fairly stable, and still further to the right we find the " B group " metals which are normally active, although in several cases (copper and zinc) a fleeting type of passivity can be brought about by treatment with chromates.

Summary and Conclusions.

Passive iron is covered with a film which is too thin to give interference tints but which can be removed and thus rendered visible by dissolving away the metal below it by anodic treatment or by means of iodine. This film is the cause of the passivity; where the film is discontinuous or contains cracks, the iron is active. Chlorides favour the activation of passive iron, because chlorine ions can pass through the skin, and at anodic areas the metal is dissolved away below the membrane, which becomes loosened; mere immersion in a chloride solution, under conditions which preclude the flow of local currents, does not necessarily cause passive iron to become active. The attack on passive iron is often localised at the water level, where the film readily becomes loosened. Nitric acid is an untrustworthy reagent for producing passivity on iron, but the phenomena produced by it are probably to be ascribed to film formation, although in this case a film has not actually been isolated. Passive copper and aluminium are covered with transparent films, which have been obtained in flakes; the behaviour of these metals is in many ways analogous to that of iron, although in copper the passivity is less persistent than in iron, whilst in aluminium it is more persistent.

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