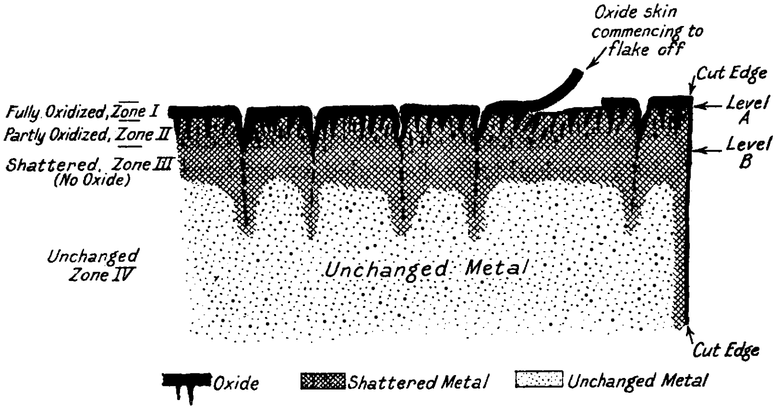
CCCLV.—*The Passivity of Metals. Part III. The Quantity and Distribution of the Superficial Oxide.*

By ULICK R. EVANS and JOHN STOCKDALE.

PREVIOUS work by one of us (Evans, J., 1927, 1022; this vol., p. 92; *Nature*, 1927, **120**, 584; 1929, **123**, 16) has indicated that the surface films of metal, isolated by undermining, consist sometimes mainly of oxide, sometimes mainly of metal, but generally of both. An interpretation is afforded by the work of Bowden and Rideal (*Proc. Roy. Soc.*, 1928, *A*, **120**, 59; *Nature*, 1928, **122**, 647), who have found that the true surface area of metals greatly exceeds the apparent area, especially after abrasion or similar treatment; presumably there is a series of invisible fissures opening on to the metallic surface, large near their mouths and narrowing as they pass inwards. When metal is exposed to air, oxygen molecules will penetrate a certain distance up the fissures, producing thin walls of oxide, but beyond a certain point penetration will cease. Where the breadth of the "fissures" becomes so small as to be comparable with the interatomic distance, the material is best regarded as shattered metal having a distorted or interrupted lattice. Such a zone will be more unstable, and therefore more quickly corroded, than the unchanged metal in the interior; but further out, where the fissures are lined by sheaths of oxide, the material will be less corrodible than the unchanged metal, since these sheaths will present at least some obstruction to the attack. Clearly the state of affairs will vary with the mechanical and chemical properties of the metal, but in general four zones are to be expected (Fig. 1): (I) An outer zone, consisting *wholly of oxide*; (II) a zone containing

FIG. 1.



oxide and metal, the proportion of metal gradually increasing as one passes inwards—this zone should have an abnormally *high resistance to attack*; (III) a shattered zone, *fairly free from oxide*, and having an abnormally *low resistance to attack*; (IV) the *unchanged metal* forming the main interior portion.

At low temperatures, any passage of oxygen below the main surface will occur largely through the fissures, but as the temperature rises, diffusion through solid oxide becomes more rapid, and Zone I will gradually thicken at the expense of Zone II and finally of Zone III; at elevated temperatures, the inner boundary of Zone I is likely to be fairly straight, but the inner boundaries of Zones II and III are always likely to be ill-defined. Violent abrasive treatment is likely to increase the combined thickness of Zones I and II, and probably that of Zone III.

Evidence that the metal is specially resistant near the surface, and specially susceptible a little lower down, is to be found in the work of Bengough and his colleagues on brass (*J. Inst. Metals*, 1920, **23**, 80) and on zinc (*Proc. Roy. Soc.*, 1928, *A*, **121**, 88). Moreover, the early " iodine method " of removing thin oxide films (Evans, J., 1927, 1024) undoubtedly depended on preferential dissolution along Zone III. But in this case the long immersion in the iodine was capable of dissolving away a great deal of the residual unchanged metal in Zone II of the separated film. By employing a modified anodic method of dissolving away Zone III, it has now been found possible to preserve most of the residual metal in Zone II, since as soon as the surface films are brought out of effective electrical contact with the basis, dissolution will cease; precautions are obviously needed to prevent secondary changes, such as rusting.

EXPERIMENTAL.

Methods as applied to Nickel and Copper.—The electrolytic apparatus is a simple U-tube, with some glass beads in the junction of the two limbs, filled with saturated potassium chloride (for nickel) or sulphate (for copper). The specimen to be stripped is made the anode in one limb, whilst a cathode of the same metal is placed in the other; the metallic chloride (or sulphate) formed in the anodic limb reacts with the alkali from the cathodic limb to produce a " natural " diaphragm of membranous hydroxide.

Under suitable conditions, corrosion penetrates behind the surface film, which becomes quite loose. For a nickel strip heated to give a first-order tint, with breadth 2 cm., immersed depth 1 cm., and having its back protected with varnish, an appropriate current is 0·16 amp.; this causes loosening in about 10 minutes. The colour quickly disappears from the front, and slight local bulgings appear at the bottom; these gradually extend upwards, and finally the whole surface becomes wrinkled and appears to be covered with a loose folded skin. The bulgings and wrinkling strongly suggest that the oxide-skin has a " natural area " greater than the metal, and is in a state of compression when attached to the basis (compare Pilling and Bedworth, *J. Inst. Metals*, 1923, **29**, 529).

The exact degree of loosening found to be suitable for the next operation varies somewhat with the metal, but no attempt is made to dissolve away the whole of the metal within the skin, as in the original anodic method (Evans, J., 1927, 1022). When a suitable state has been reached, the electrode is taken out and pressed on to a glass surface, previously covered with " clear Belco " (a nitrocellulose lacquer) which has been allowed to dry sufficiently to reach a " tacky " condition. The loosened skin then leaves the metal, being transferred to the lacquered surface, and can be washed and dried. This method will be called the " transfer method."

For many purposes, it is convenient, instead of transferring the film on to glass, to swirl the electrode in clean water; the loosened skin then peels off in loose curling flakes, which sink to the bottom and can be washed by decantation. This will be called the " loose-flake method."

If a square piece of abraded sheet nickel is heated along one edge, so as to produce the usual sequence of interference tints, the unheated edge remaining uncoloured, and the oxide film is then removed to a glass support by the transfer method, it will be seen to be thick at the heated edge, becoming gradually thinner as the unheated edge is approached. The film from the untinted portion, " invisible " whilst on the metal, is easily visible when stretched on the transparent support, and is almost entirely oxide, being remarkably free from metallic inclusions; evidently on nickel, the line of demarcation of metal from oxide appears to be fairly sharp. This is the only easy way of separating the " invisible " film from ground nickel, since unless it is connected laterally to a thicker film, the thinner film is only removable with extreme difficulty.

When the same experiment is repeated with copper, a similar film of gradually altering character is obtained, but the low-temperature portions contain much residual metallic copper; the proportion of metallic copper to oxide gradually diminishes as the high-temperature edge is approached. Evidently on copper the demarcation line between oxide and metal is not sharp, as on nickel, but an intermediate zone of interlocked metal and oxide occurs, as suggested in Fig. 1.

Some measurements of the oxide removed from a given area of heat-tinted nickel by the transfer method have been made, the nickel present being estimated by Rollet's modification of the glyoxime method (*Compt. rend.*, 1926, **183**, 212); the estimation is not very satisfactory, but the numbers agreed within experimental error with Constable's values (*Proc. Roy. Soc.*, 1928, *A*, **117**, 376).

The films stripped from heat-tinted nickel themselves showed interference colours when mounted on nitrocellulose, and, unlike copper and iron oxide films, they had no inherent colour to complicate the question. Thus nickel oxide appears to be a suitable case wherewith to test the validity of an assumption which has frequently been made by those who have used interference colours to measure the velocity of film growth. It has usually been assumed that to obtain the thickness of a film it is only necessary to divide the thickness of the air film needed to give the same colour by the refractive index of the material. The optical reasoning underlying this assumption appears open to question, and the argument becomes invalid if the colour of the stripped oxide film is not complementary to that of the film on the metal. Mr. S. C. Britton has kindly stripped a number of nickel specimens tinted to different colours and has compared the colours of the unstripped and stripped films. The correlation given in the following table indicates that, although the two sets of colours are often nearly complementary, yet this is definitely not the case with nickel tinted to the second-order yellow.

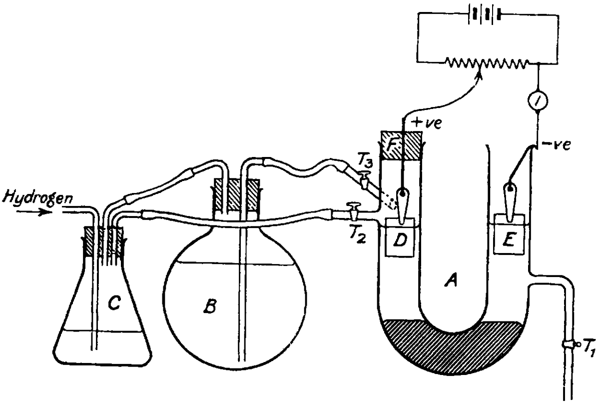
Colour (by reflected light) of	
metal with film attached.	stripped film.
Yellow I	Silvery (faintly bluish)
Mauve I	Silvery
Dark blue I	Silvery
Light blue I	Yellowish-silver
Silver (" Hiatus zone ")	Yellow, becoming pink
Yellow II	Fine mauve (red rather than blue)
Red II	White (faintly greenish)

Independent evidence that the assumption mentioned above is inexact is provided by microgravimetric estimation of the mean thickness of silver iodide films (Evans and Bannister, *Proc. Roy. Soc.*, 1929, *A*, **125**, 370).

Methods as applied to Iron.—In treating iron, the cathodic limb of the **U**-tube was kept filled with hydrogen to avoid contamination with secondary ferric hydroxide. For quantitative purposes, a different apparatus was used (Fig. 2). The **U**-tube (*A*) had three side tubes, fitted with taps. Tap T_3 led to a 3-litre reservoir *B* (not drawn to scale) containing air-free water, which was connected, through flask *C* containing dilute soda, to a Kipp's hydrogen generator. The tap T_2 connected the **U**-tube direct to *C*, and tap T_1 was used to control the washing process. The anode *D* was held in place by a metal clip soldered to a stout copper wire making a tight fit in the rubber stopper *F*, while the cathode *E* hung loosely from the side of the cathodic limb; the electrodes were connected through an ammeter and rheostat as shown. The procedure during an experiment was as follows.

The taps T_1, T_2, and T_3 are closed; the U-tube is filled with electrolyte to the required level, and a few crystals of ferrous sulphate are dropped into the solution in the cathodic limb. The ferrous solution so produced serves to take up the alkali as soon as it is formed during electrolysis, and confines precipitation to a small zone round the cathode and above the opening of the exit tube. The mouth of the cathodic limb is made temporarily air-tight by fitting it with a rubber stopper, and the tap T_2 opened to allow a brisk flow of hydrogen to displace the air in the anodic limb; while T_2 is still open, the stopper *F*, with the specimen attached, is placed in position. T_2 is then closed, the stopper in the cathodic limb is replaced by the cathode, and the necessary electrical connexions are made. When anodic treatment is finished, the cathode is again replaced by a stopper, and the tap T_3 is opened. (The back surface of the anode is protected by nitrocellulose varnish and the wash-water inlet, shown dotted, is placed opposite this surface so that eddies due to the flow of water are checked by the anode itself, thus minimising the risk of breaking the film.) The wash-water in *B* is under pressure from the Kipp's apparatus, and its rate of flow into the U-tube is controlled by the tap T_1. When washing is complete, tap T_3 is closed and the anode removed carefully. The film is stripped by washing the anode gently with a jet of boiling water or by swirling it in freshly boiled water. The flakes so obtained are dissolved immediately, under an atmosphere

FIG. 2.



of carbon dioxide, in the requisite quantity of hydrochloric acid; this quantity is governed by the approximate thickness of the film and the acidity of the standard solution against which it is to be matched by the thiocyanate method.

In order to ascertain whether reasonably thorough washing of soluble iron salt from the flakes was possible, the following experiment was performed. A nickel anode with its film previously loosened, but still clinging, was introduced into the **U**-tube of the apparatus just described after the operation of separating an iron film. The nickel film was then washed, removed, dissolved, and the resulting solution tested for iron; the iron found was not appreciably more than in a blank experiment, the small amount present being derived as an impurity from the nickel.

Electrolytic iron, E 28, ground with French emery No. 000, and heat-tinted to the first-order yellow, yields two distinct types of flake, according to the manner of removal. (1) If the edges are freshly trimmed just before the experiment, so as to allow the anodic attack access to Zone III, fairly thick flakes are obtained, with some definite spots of residual metal of various sizes, as shown up by the ferricyanide method (Evans, *Nature*, 1927, **120**, 584); these display a curious brownish colour, possibly due to particles of residual metal too small to be individually visible under the microscope. Various estimations by the thiocyanate method of flakes taken from measured areas indicated the iron oxide present to be 5·2, 5·0, 4·7, and 5·0 × 10^{-5} g. per sq. cm. (2) On the other hand, when the edges of the specimen are protected by nitrocellulose varnish, the separation occurs much more quickly, yielding much thinner films, highly transparent, much less brown, and free from particles of residual metal; these seemed to be practically entirely oxide; estimations gave 2·6, 2·5, 2·1, and 1·6 × 10^{-5} g. of ferric oxide per sq. cm. The isolation of this thin type of film appears to be due to a form of attack which commences at weak points in the surface film I, and penetrates quickly along level *A* at the interface between Zones I and II. The failure of the oxide skin is presumably due to the state of compression, which is only relieved if the oxide breaks away from the base; the separation will therefore tend to follow the bottom boundary of Zone I. Occasionally separation occurred along this level even when the edges were not intentionally protected, whilst in one case a specimen with protected edges produced flakes of intermediate character, with 3·1 × 10^{-5} g. of oxide per sq. cm., the time of separation and appearance of the metallic basis being also intermediate between the two ordinary types.

The correctness of the explanation of the separation at the higher level is indicated by the fact that iron heated rather more strongly, so as to give a mauve interference colour, yielded practically the same type of film whether the edges were protected or not; evidently the uniform oxide layer, produced by diffusion through solid oxide, has penetrated sufficiently deep to eliminate Zone II almost completely. The amount of oxide separated from mauve specimens with unprotected edges averaged $5{\cdot}5 \times 10^{-5}$ g. per sq. cm., and with protected edges, $5{\cdot}2 \times 10^{-5}$ g. per sq. cm. The phenomenon of separation at two distinct levels is only obtained on iron when tinted to yellow thicknesses; but copper shows separation at different levels when heated below the interference colour range; the films obtained by undercutting from the edges contain more residual copper than those obtained from the face.

The microscopic aspect of the iron base after stripping is quite different accordingly as the separation has proceeded near the surface (along level *A*) or further down (along level *B*). In the first case, the basic metal is left smooth (light to the naked eye), and in the second deeply pitted (black to the naked eye). The fact that the time of electrolysis needed for separation in the first case is much shorter (5—30 mins.) than in the second case (1¼—2 hours) is easily understood. For, in the first case, advantage is taken of the natural flaking off of the film, and comparatively little anodic corrosion of metal is required; whilst in the second case, considerable destruction of metal is needed before loosening is possible.

It should be noted that removal at the lower level (*B*) will probably give the more accurate measure of oxide per unit area, although even here the accuracy leaves much to be desired. The separation at the higher level agrees better, however, with the "optical method" of estimating thicknesses as used by Constable, giving an average value of $2{\cdot}2 \times 10^{-5}$ g. of oxide per sq. cm. Constable's measure of the film on yellow-tinted iron ($0{\cdot}46 \times 10^{-5}$ cm.) is equivalent to $2{\cdot}36 \times 10^{-5}$ g. of oxide per sq. cm., if the specific gravity of ferric oxide is assumed to be 5·13, or to $2{\cdot}43 \times 10^{-5}$, if the specific gravity is taken as 5·29, a value found for the scale formed at very high temperatures by Pfeil (*J. Iron Steel Inst.*, 1929, **119**, 501). Actually the numbers found by this optical method are not strictly measures of the total oxide present, since the thickness obtained will be the depth at which there exist sufficient blocks of unchanged metal to form a reflecting surface for light; this depth will vary from point to point, explaining the broadness of Constable's absorption bands; a uniform film should give a narrow absorption band. Marked divergences between the oxide thicknesses as estimated from colour observation or from weight increment have been obtained by Tammann and Bockow (*Z. anorg. Chem.*, 1928, **169**, 42).

It is easy now to understand the fact observed in previous work on iron and copper with the older methods of separation, *viz.*, that residual metal is almost absent from the oxide films separated from specimens tinted to Blue I or greater thicknesses, but is increasingly present in the films where the oxidation has been less.

Electrolytic iron abraded with No. 000 French emery, immersed for 24 hours in potassium chromate, and subjected to anodic treatment with protected edges, yielded a layer containing much residual metal; two estimations of the oxide present after stripping indicated $2{\cdot}9 \times 10^{-5}$ and $3{\cdot}5 \times 10^{-5}$ g. per sq. cm. Whether these numbers represent accurately the oxide present before stripping is perhaps still a little doubtful. Every possible precaution was taken to prevent oxidation during stripping, but, in spite of several attempts, no trustworthy *independent* method could be devised to check the numbers.

Early work had indicated that " stainless steel," with surface as forged, suffered on anodic treatment undercut pitting; the undercutting was at a fairly deep level which left an opaque surface layer of metallic appearance. It has now been found possible, by long anodic treatment of stainless steel abraded with fine emery, to obtain, in addition to opaque flakes, a very thin transparent skin, carrying striæ representing the original abrasive treatment; this resembles the thinnest nickel oxide films, and is free from the brown colour characteristic of films from pure iron. In some materials, where the oxide layer is very thin, the skin left is essentially metallic in appearance. " Staybrite " (iron with 18% chromium and 8% nickel), treated as a rolled strip 1·5 mm. thick, 8 mm. broad, and immersed to a depth of 15 mm., after 6 hours' anodic treatment at 0·05 amp., suffered complete internal corrosion, but left an envelope representing the surface layers; this envelope, apart from numerous holes, retained the original shape of the specimen, but, unlike the envelope from passive iron previously described (J., 1927, 1022), the material was quite opaque and retained a bright silvery lustre. Similar results were obtained from staybrite which had been wire-brushed or filed, and then exposed to air before anodic treatment.

Comparative Ease of Stripping of Different Materials.—A number of new film separations have been attempted, including several materials not previously studied; in most cases the surface was abraded with French emery No. 1 before oxidation, but some interesting results were obtained from wire-brushed specimens, the film showing a characteristic dappled appearance reproducing the abrasive treatment. The difficulty of removing the skins varied enormously in different cases; in some instances, no removal could be effected at all; in others, the skin came away at a few points only; in others it came away quickly and cleanly in large pieces. With a few exceptions it may be said that "protective" films were more difficult to remove than "non-protective" ones, as might perhaps be expected, whilst thin films were more difficult to separate than thick ones. Thus, whilst iron and copper exposed to air at ordinary temperatures yielded separable films, it was difficult to obtain the corresponding films from nickel. Where the metals with highly protective skins proved amenable to treatment at all, they usually furnished films with so much residual metal as to be opaque; an example (staybrite) has already been mentioned. Other conditions being equal, a sharp boundary between the oxide and metal, with absence of the mixed Zone II, facilitated removal; thus films were much easier to remove from heat-tinted nickel than from heat-tinted iron, although the reverse was true of the unheated metals. Coarse abrasion was found to militate against easy removal. The presence of a second phase (which must clearly interrupt the continuity) acted in the same way; thus whilst electrolytic iron (E 28) abraded with French emery No. 1 and exposed to air for various periods (10 secs. to 24 hours) readily gave films, mild steel (H 26) treated in the same way gave no films or only small fragments; the same steel when heat-tinted gave films, but the reluctance to leave the metal increased as the films became thinner.

After immersion in $M/2$-potassium chromate solution for various periods from 15 mins. to 24 hours, this same steel (H 26) gave films in fairly clear flakes; this is understandable, since chromate treatment is believed to give thicker films than exposure to air; indeed, as found previously (Evans, *J. Soc. Chem. Ind.*, 1925, **44**, 163T), some steels after long immersion in chromate actually show interference colours. Nickel also gave films far more readily after chromate treatment than after exposure to cold air. On the other hand, a second steel (H 28) did not give films after chromate treatment; this may have been due to the higher contents of carbon and silicon (0·26 and 0·15%, as against 0·18 and 0·04% for H 26), but physical differences may also be responsible; thus, different rolling and annealing treatment of a given nickel sample were found greatly to affect the ease of separation of films from the heat-tinted metal.

The recent work of Rideal and Wansborough-Jones (*Proc. Roy. Soc.*, 1929, *A*, **123**, 202) has suggested that oxygen will react without activation with any metal whose thermionic work function is less than 3·6 volts; thus "base" metals should oxidise readily in air at ordinary temperatures, whilst "noble" metals will oxidise only at high temperatures, or in the presence of a powerful oxidising agent. Nickel, with a work function of 4·05 volts, is rather near the border-line; and after exposure to air at ordinary temperatures, its film would probably be thin or even absent, but exposure to hot air or to oxidising agents might produce a film thick enough to be separable. This may explain the differences actually noted between the behaviour of nickel and iron.

The differences in ease of separation of films from different materials, or the same material differently treated, were quite reproducible when emery-ground surfaces were used, and were so marked as to form an important index of the character of the material.

Summary.

A new method for the removal of the surface skins of metals, dependent on anodic undermining, has been worked out with a view to preserve the metal enclosed in the layer of oxide; it is often possible to transfer the film to glass coated with nitrocellulose. Films have been removed from several fresh materials, such as nickel and carbon steel, whilst a transparent skin has now been isolated from "stainless steel." The oxide on heat-tinted nickel appears to be sharply divided from the metal, whilst on copper and iron there is interlocking. Some determinations of the oxides per unit area have been made. On yellow-tinted iron, undermining can be carried out at either one of two different levels; undermining at the upper level yields a transparent film consisting of oxide alone in an amount agreeing fairly well with Constable's optical determinations, whilst undermining at the lower level gives a film with a greater amount of oxide and considerable amounts of metal. The difficulty of film removal varies enormously in different cases, and is usually greatest when the film is very thin and highly protective; but it is also increased when the continuity is interrupted by coarse abrasion or by the presence of heterophase impurities.

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