CLXXVII.—*The Passivity of Metals. Part V. The Potential-Time Curves of Some Iron Alloys.*

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PREVIOUS work (Evans and Stockdale, J., 1929, 2651) having shown that those oxide films which give the best protection are the most difficult to remove, it seemed necessary to develop a method of studying the character of such films whilst they were still adhering to the metal. The most promising scheme was based on an examination of time-potential curves similar to those obtained by May (*J. Inst. Metals*, 1928, **40**, 141), by McAulay and Bastow (J., 1929, 85), by W. J. Müller and Konopicky (*Monatsh.*, 1929, **52**, 463), and by Speller (private communication). Such curves have already been studied by one of us (Evans, J., 1929, 92), but the method employed allowed the liquid to have access to the cut edges of the vertical specimens, causing complications due to shearing stresses and exposure of the interior layers, which in rolled metals may differ physically and chemically from the face; furthermore, the inconveniently rapid movement of the potential made it difficult to obtain early values.

A new method has now been worked out in which specimens are placed horizontally and arranged so that their edges do not come into contact with the liquids. The potential movement is here comparatively slow. An improved method of measuring the potential has also been adopted, and in this way a study has been made of the behaviour of different varieties of iron with or without carbon, copper, nickel, chromium, and molybdenum; a few experiments have also been carried out with aluminium.

EXPERIMENTAL.

Materials.—The iron E 28 and steel H 28 were kindly presented by Dr. W. H. Hatfield and the steels K 1 and K 2 by Mr. Taylerson, of

Pittsburgh, Pa.; K 1 is a typical American copper steel. In considering the analyses given below, it should be remembered that practically all commercial irons contain copper, and that amounts below 0·05% are usually recorded in routine analysis as " traces."

	E 28.	H 28.	K 1.	K 2.
Carbon	0·03	0·26	0·055	0·11
Silicon	Trace	0·15	0·010	0·010
Sulphur	0·005	0·014	0·052	0·037
Phosphorus	0·020	0·018	0·078	0·060
Manganese	0·04	0·57	0·31	0·51
Copper	Nil	0·045	0·187	0·052
Thickness (mm.)	0·34	0·32	0·86	0·86

In addition a sample of " Staybrite " steel, an austenitic alloy with 18% of chromium and 8% of nickel, was the gift of Dr. W. H. Hatfield, whilst Mr. J. H. G. Monypenny very kindly provided specimens of the following alloys :

	Cutlery " stainless steel."	" Stainless iron."	" Two-score."	" Anka."	" B.B.4K."
Carbon	0·27	0·09	0·12	0·12	0·13
Silicon	0·19	0·22	0·40	0·24	0·54
Sulphur	0·045	0·033	0·032	0·033	0·052
Manganese	0·17	0·19	0·82	0·18	0·13
Chromium	13·2	13·6	17·4	15·6	17·2
Nickel	0·20	0·36	2·15	10·5	10·1
Molybdenum	—	—	—	—	3·42
Tempering temperature	750°	700°	650°	—	—
Thickness (mm.)	2·21	1·66	1·66	2·18	1·19

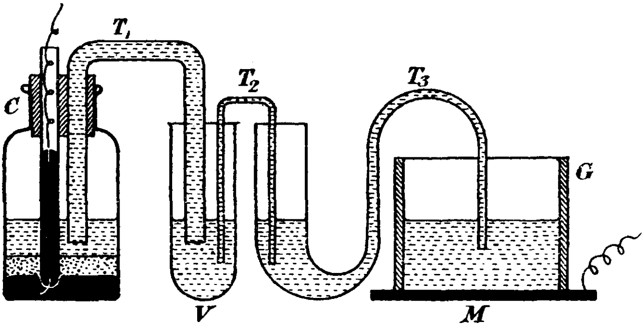
Of these, " Anka " and " B.B.4K " had been heated to 1000—1050° and air-cooled; the structure was wholly austenitic. The others were " hardenable " steels, softened, after rolling, by tempering at the temperature indicated; these exhibited a duplex structure, with carbide as minute particles distributed in the ferrite.

The aluminium was of two types : (*a*) electro-refined sheet (soft) with 0·013% of silicon, 0·012% of iron, 0·014% of copper, and 0·004% of titanium, kindly supplied by Mr. E. H. Dix of the Aluminum Company of America, and (*b*) some soft sheet of British origin containing 0·33% of silicon and 0·40% of iron.

Procedure.—The materials E 28 and H 28 were ground with French emery paper No. 1. For the harder materials, grinding on a coarse wheel was necessary. In some cases, this was followed by grinding with successively finer grades of emery, ending with French No. 1; this will be called " sequence-finish." After abrasion they were degreased with carbon tetrachloride. A glass cylinder of 3·5 cm.

diameter and 3 cm. height (G, Fig. 1), ground flat at the bottom, was cemented on to the metal (M) by means of nitrocellulose solution, and the whole was exposed to air for a week, with protection from dust and moisture. The calomel electrode C and connecting tubes T_1, T_2, and T_3 were then placed in position. The whole was introduced into an outer glass vessel surrounded with a water jacket, itself heavily lagged. This vessel contained a dish of $3N$-sodium hydroxide —the concentration shown by Mitsukuri (*Sci. Rep. Tôhoku Imp. Univ.*, 1929, **18**, 245) to be the most efficient in absorbing traces of acid fumes. In the potassium chloride experiments, all the tubes and vessels contained $M/10$-potassium chloride (that in C and T_1 being saturated with calomel). In the potassium chromate experiments, T_2, T_3, and G contained $M/10$-potassium chromate, whilst saturated potassium chloride was used in V; some care was necessary to exclude traces of chloride from G, or low values were obtained.

FIG. 1.

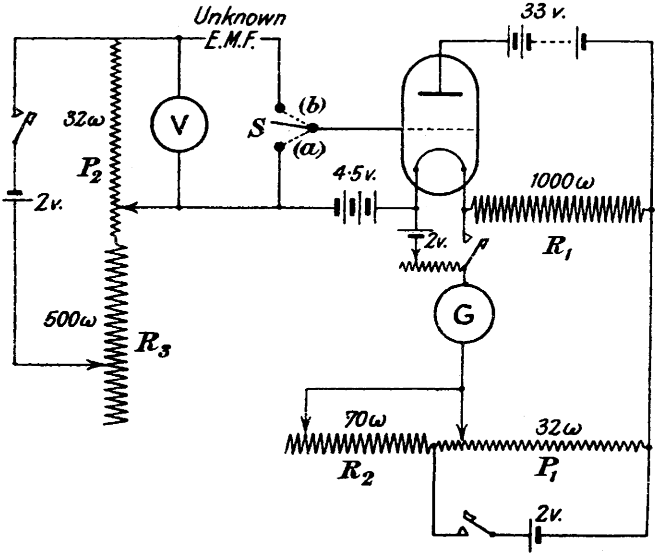


All the tubes and the vessel V were filled before shutting up the outer vessel, but the liquid was only introduced into G through a vertical tube at the start of the experiment proper; the depth of the liquid was 1·8 cm. and the bottom of the tubulus was about 1 cm. above the metal.

The arrangement for measuring the potential is shown in Fig. 2. It depends on the principle employed by May (*loc. cit.*), modified to give increased sensitivity; the valve employed was Mullard No. PM 252. When the switch S is in position (*a*), the grid bias is 4·5 volts, and a small current flows through the anode circuit and causes a fall of potential over the resistance R_1, producing a deflexion to right or left on the detector G; the potentiometer resistance P_1 is adjusted until this deflexion vanishes. A movement of the switch S into position (*b*) brings the *E.M.F.* to be measured into the grid circuit, and by altering the grid bias, causes again a deflexion on G. The potentiometer resistance P_2 is then moved until the deflexion on

G is again zero, which will clearly be the case when the potential drop on P_2 is exactly equal and opposite to the $E.M.F.$ to be measured; this value can then be read directly on the voltmeter V. Practically no current passes through the experimental cell, even when the apparatus is out of adjustment. The use of the shunt resistance R_2 and the series resistance R_3 was necessary to obtain the required fine adjustment.

FIG. 2.



A list of experiments performed is shown in Table I, together with the general form of the curves, and the value of the (hydrogen scale) potential after 2 hours (it was usually fairly constant after this time); the temperature was 15°. Some of the curves are shown graphically in Figs. 3 and 4. The time scale of the two diagrams is different, and on Fig. 4 it has been necessary to omit some of the early points, but these all lie on the curves. The potentials are expressed on the normal hydrogen scale, and the times measured from the moment of introduction of liquid. The measurements were usually continued for 3 hours. Table I shows that after 2 hours the values reached in duplicate experiments were generally much the same, but there was often rather more discrepancy between the earlier parts of the curves, where the potential was fluctuating in an irregular manner.

The Significance of the Potential of Film-covered Metal.—The potential of a metal covered with a discontinuous oxide film will in general be intermediate between the values given by uncoated metal and by solid oxide; the more porous the film is, the nearer will the

TABLE I.

Expt. No.	Material.	Treatment.	Liquid.	Nature of curve.	Potential.
0	Iron E 28	Coarse wheel alone	$M/10$-KCl	Falling	−0·410
1, 2	,,	French emery No. 1	,,	,,	−0·405 −0·410
3, 4	Steel H 28	,, ,,	,,	,,	−0·420 −0·420
5, 6	Iron E 28	,, ,,	$M/10$-KCl + $M/10$-K_2CrO_4	,,	−0·260 −0·240
7	Steel H 28	,, ,,	,,	,,	−0·248
8	Iron E 28	,, ,,	$M/10$-K_2CrO_4	Initial rise	+0·308
9, 10	Steel H 28	,, ,,	,,	,,	+0·310 +0·293
11, 12	Steel K 2	Sequence *	$M/10$-KCl	Falling	−0·470 −0·460
13, 14, 15	" Copper steel " K 1	,,	,,	,,	−0·450 −0·450 −0·480
16, 17	" Stainless iron "	Coarse wheel alone	,,	Initial fall	−0·155 −0·173
18, 19	Cutlery " stainless steel "	,, ,,	,,	,,	−0·193 −0·205
20, 21	,, ,, ,,	Coarse wheel, then nitric acid (*d* 1·20)	,,	,,	−0·190 −0·218
22, 23	" Two-score "	Coarse wheel alone	,,	Nearly level	−0·073 −0·118
24, 25	,,	Sequence *	,,	Initial irregularity, then nearly level	+0·170 +0·170
26	" Anka "	Coarse wheel alone	,,	Slight initial fall	+0·028
27, 28	" B.B.4K "	,, ,,	,,	Initial irregularity, then level	+0·123 +0·106
29	" Staybrite "	Wire-brushed	,,	Initial fall	−0·023
30	,,	Wire-brushed, annealed	,,	Initial rise	−0·033
31	,,	As 30, but oxide removed	,,	Falling	−0·188
32	,,	Wire-brushed, then nitric acid (*d* 1·20)	,,	Initial fall	+0·035
33	,,	Sequence *	,,	,,	+0·128
34	,,	Sequence,* annealed	,,	,,	−0·172
35	,,	As 34, but oxide removed	,,	,,	+0·078
36	,,	Sequence,* then nitric acid (*d* 1·20)	,,	,,	+0·163
37	,,	Highly polished	,,	Gradual rise	+0·510
38	Aluminium (*a*)	Wire-brushed	,,	Initial rise	−0·452
39	,,	French emery No. 1	,,	Nearly level	−0·435
40, 41	,,	Cold-rolled	,,	,,	−0·424 −0·445
42, 43	Aluminium (*b*)	French emery No. 1	,,	Very gradual rise	−0·425 −0·425

* " Sequence " indicates abrasion on the coarse wheel, followed by grinding with emery of diminishing coarseness, ending with French No. 1.

potential be to the value for uncoated metal (W. J. Müller, *Monatsh.*, 1929, **52**, 221; Evans, J., 1929, 104). With a highly porous film,

FIG. 3.

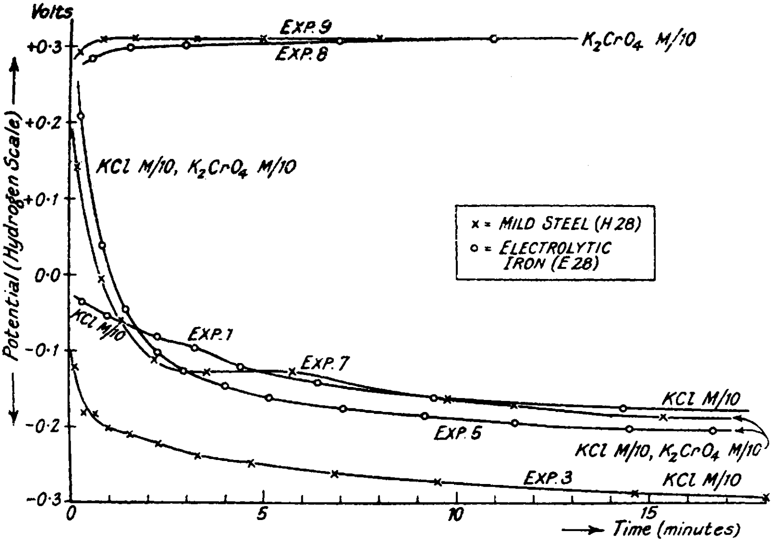
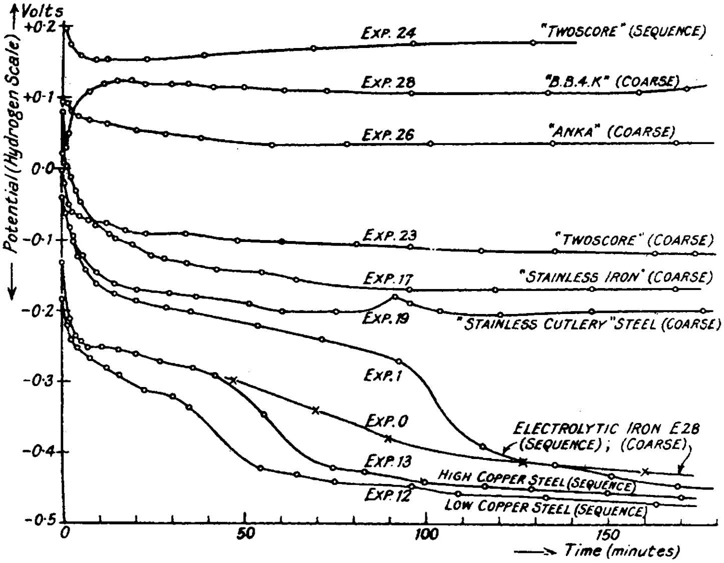
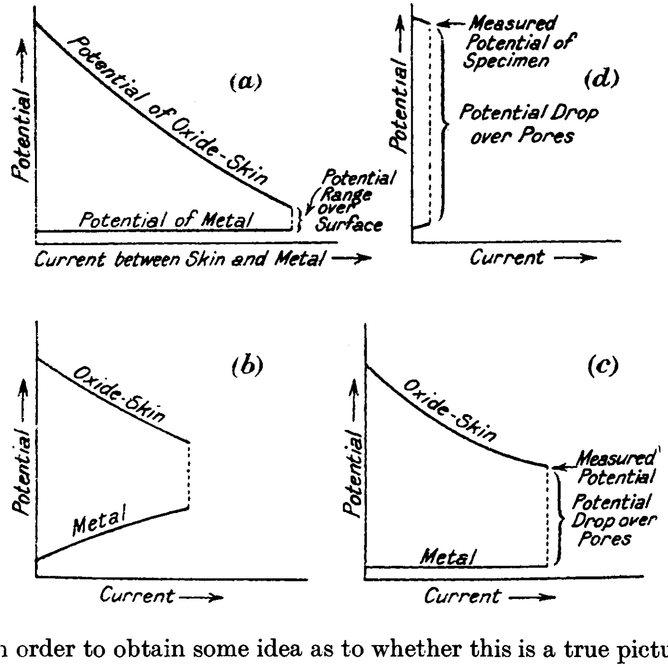


FIG. 4.



the resistance of the short-circuited cell, metal | electrolyte | oxide, will generally be low, and the minute local currents that pass between the oxide skin as cathode and any accessible metal as anode will be regulated by polarisation, and particularly by the amount of dissolved oxygen (depolariser) reaching the oxide skin. In general, we may expect the potential at the oxide (cathodic) surface to descend with current flowing until it nearly meets the anodic potential, as indicated in Fig. 5(*a*); the slight difference of potential remaining when the " rest-strom " is passing is that needed to force this weak current through the small ohmic resistance of the circuit. In some cases the anode potential may rise to meet the cathodic potential, as in Fig. 5(*b*).

FIG. 5.



In order to obtain some idea as to whether this is a true picture of the process, an experiment was performed in which, instead of a porous oxide film, a coat of a " noble " metal pierced by a hole was used. A sheet of iron was ground, and covered with a pierced sheet of copper, which was insulated from it with paraffin wax; the whole was covered with $M/10$-potassium chloride. The potentials were measured against two calomel electrodes, the tips of the two tubuli being almost in contact with the two metallic surfaces. Whilst electrically insulated, the two metals showed very different potentials (+ 0·083 volt for copper and — 0·102 volt for iron); but when put into electrical contact, the copper potential fell whilst the iron potential rose, so that the whole bi-metallic specimen became practically equipotential, the value being + 0·048 volt at the copper surface and + 0·043 volt at the iron. Other experiments confirmed this; the time needed for the mutual approach of the two values varied considerably with the conditions.

The value of the " compromise " potential reached by a bi-metallic system depends on the relative areas of the two metals. An iron sheet was inserted vertically in $M/10$-potassium chloride, and the tip of a narrow copper strip was allowed just to touch the liquid. The potential of the iron was − 0·317 volt and of the copper + 0·098 volt; they were joined, and the copper potential at once fell to − 0·322 volt, the value then shown also by the iron. Here the anodic area is large compared with the cathodic area, and only the cathodic polarisation is important. The conditions were then reversed by using a copper sheet and the tip of a narrow iron strip. Here the potentials were − 0·217 volt for the iron and + 0·118 volt for the copper before the connexion; after short-circuiting, the values moved to − 0·092 volt for the iron and + 0·048 volt for the copper, whilst 6 minutes later the values were respectively − 0·057 and − 0·037 volt—a difference of only 20 millivolts.

It has often been assumed that the potential exhibited by a bimetallic specimen is that of the more reactive metal present; but this is only true provided that, in the short-circuited cell produced, (*a*) the cathodic greatly exceeds the anodic polarisation, and (*b*) the resistance is negligible; under such conditions, the cathodic potential will drop almost to the original anodic value. When the anodic area is very small, the rise in the anode potential, as measured, is quite considerable; it is uncertain whether this measured rise is due to a *real* anodic polarisation or to the fact that, when the anodic area is a mere point, a considerable fraction of the ohmic resistance of the circuit falls between the tubulus and the metal, thus causing an " apparent anodic polarisation." In either case the " compromise " potential is not equal to the unpolarised potential of the reactive constituent.

Previous work (Evans, *J. Inst. Metals*, 1928, **40**, 121) has shown that when the zinc layer of zinc-covered iron is removed gradually with acid, the potential rises as the area of exposed iron increases; any value between the potential of zinc and the potential of iron is possible for the system. Similarly, when a metal is covered with a porous oxide film, it may show *any* value between the potentials of the clean metal and the solid oxide. If the oxide film is highly discontinuous, the potential measured will be practically that of film-free metal [Fig. 5(*a*)]. If the cracks in the skin are extremely small, the measured potential will be higher; this is pictured in Fig. 5(*b*) on the assumption that a true anodic polarisation contributes to the rise in the compromise value, and in Fig. 5(*c*) on the assumption that the elevation in the measured potential is simply due to the high resistance imposed by the narrowness of the pores. If, when this stage has been reached, the breakdown extends from the original weak points, the potential will fall, first rapidly and then more slowly, as the conditions approach the limiting case pictured in Fig. 5(*a*); the shutting off of oxygen by secondary corrosion product (*e.g.*, rust) will contribute to the fall. Conversely, if repairing influences prevail, causing the pores to become narrower or less frequent, or rendering the film thicker, the measured potential will rise. The limiting case where the pores vanish and the potential becomes equal to that of a " solid " oxide electrode may not often be reached in practice; Fig. 5(*d*) suggests the state of affairs just before the pores vanish.

The potential of the metal just after immersion is of special interest. It has been shown by independent methods (Freundlich, Patscheke, and Zocher, *Z. physikal. Chem.*, 1927, **128**, 321; **130**, 289; Evans, J., 1927, 1029) that, in dry air, oxidation of iron commences very rapidly; but since interference colours never appear, even after months, it is evident that the film must quickly become impenetrable to oxygen molecules. If therefore the solution contains nothing more penetrating than oxygen molecules, it should show the oxygen potential, at least at the moment of immersion. Experiments 1 and 3 (Fig. 3) show clearly that, on chromium-free iron, even the initial potential is a comparatively low one. Evidently, the solution contains some constituents more penetrating than oxygen molecules; in the chloride solution, these are no doubt the chlorine ions, which will enter pores in the skin inaccessible to oxygen, and allow anodic attack on the metallic iron, generating ferrous chloride, the corresponding amount of potassium hydroxide being formed at the cathodic (oxide) surface outside. The ferrous chloride and potassium hydroxide will interact to give hydroxides of iron. If the pores are very small (approaching molecular size), the iron hydroxide will be produced at the mouth of the pores practically in contact with the iron, and may easily help to heal the defects in the original skin; thus, in some of the iron alloys where the potential is high at first, the potential actually rises (see Fig. 4, Expt. 28). Where the cracks are considerable at first, however, the iron hydroxide will generally be precipitated at a sensible distance as a loose membrane, which will not be protective; indeed, it may actually stimulate the attack by excluding oxygen. Thus in most of the irons and steels which show low initial potentials, the potential drops with the time (see Fig. 3, Expts. 1 and 3).

It will be noticed that chromium-free iron and steel, which show falling potentials in chloride solution, show rising potentials in chromate solution (Expts. 8 and 9); here the most penetrating anion present will be the hydroxyl ion, and any anodic attack must lead to the production of ferrous hydroxide, which will be oxidised immediately to ferric hydroxide. Thus a sparingly soluble substance is formed actually in contact with the metal, which will tend to repair the damage, however extensive it may be at the moment of immersion. This explains the rise of potential with time. If chlorides are present as well as chromates (Expts. 5 and 7), the initial potential is much the same as with chromate alone, but it falls with time, instead of rising, soon dropping to a value similar to that given by chloride solution free from chromate. But, whereas a second fall occurs after about an hour in pure chloride solution, this is prevented by the presence of chromates, so that a higher final value is obtained.

It will be noticed that the rôle assigned to chromate, and also to dissolved oxygen, is not to act directly on the exposed metal; it is highly unlikely that either type of molecule could enter pores inaccessible to gaseous oxygen. Their function seems to be to act as cathodic depolarisers at the external surface of the film, thus maintaining the current and causing a flow of anions (Cl' or OH') into the pores, which will produce either repair or extension of the damage, according to circumstances.

Comparison of the Curves given by Different Materials in M/10-*Potassium Chloride.*—The ferrous materials may be divided into three classes :

I. Pure irons and carbon steels, with or without copper, which are rusted freely by "ordinary waters."

II. " Stainless " irons or steels, with about 13% of chromium, which are not rusted by ordinary waters.

III. High-chromium alloys, which resist many chemicals that attack Class II.

It is noteworthy that all the materials of Class I show rather low initial potentials, and the curves fall rapidly, finally reaching values below $-$ 0·4 volt. Those of Class II show higher initial potentials, but fall to final values of about $-$ 0·2 volt. The resistance alloys of Class III show distinctly higher values, and, in spite of some irregularities in the early stages—doubtless due to local breakdown and subsequent repair—maintain these well. It would seem that, on alloys rich in chromium, the skin formed by the direct action of air can protect the material from the moment it enters the liquid. A comparison between Expts. 26 and 27–28 seems to suggest that molybdenum further improves the quality of the skin, although the two alloys involved have not quite the same chromium content; this accords with measurements of corrosion velocity by Rohn

(*Z. Metallk.*, 1926, **18**, 387) and Endo (*Sci. Rep. Tôhoku Imp. Univ.*, 1928, **17**, I, 1251).

It was noticed that, in general, those steels which attained a final value above about 0·0 volt gave no rust at the end of 3 hours, whilst those which showed negative potentials produced rust; the "stainless" steels with potentials about − 0·2 volt yielded far less rust than the chromium-free steels with potentials about − 0·4 volt.

Expts. 12 and 13 (Fig. 4) show that the copper steel (K 1) gives the same type of curve as the ordinary carbon steel low in copper, and although the values in the middle stages appear to be somewhat higher, the final values are about the same. Two comparative experiments with K 1 and K 2 steels (respectively high and low in copper) yielded the same potential after one week; at this time, even removal of the rust and renewal of the liquid only produced a temporary rise in the potential, which at once began to fall again. This accords with the general belief that copper does not directly increase the resistance of steel towards chloride solutions under "immersed" conditions. Copper steels do not belong to the same class as chromium steels, and are not to be regarded as non-rusting or even slow-rusting materials; it is probable that the difference of behaviour of high-copper and low-copper steels shown in atmospheric tests in America (*Proc. Amer. Soc. Test. Mat.*, 1928, **28**, I, 151) is due to secondary changes in the rust after its formation, or to redeposition of copper, as indicated by the work of Carius and Schulz (*Mitt. aus dem Forschungs-Inst. der Vereinigte Stahlwerke A. G.*, 1929, **1**, 177).

All the materials of Class I show (*a*) an initial rapid drop, followed by (*b*) an arrest, (*c*) a further drop to (*d*) a final constant value. The second drop (*c*), well shown in Expts. 1, 12, and 13 (Fig. 4), was perhaps due to the formation at this stage of a definite precipitate of ferric hydroxide which settles on the metal, and definitely shuts out oxygen from certain parts (in the early stages, there is only a colloidal suspension).

The effect of a second phase in favouring a breakdown is well brought out. The curves for steel H 28 descend more rapidly than those for electrolytic iron E 28, although the final value is not very different; this had been noticed for vertical specimens, and accords with the fact—established by laboratory and field tests—that the rusting of electrolytic iron develops less quickly than that of steel, although when once started it proceeds quite readily. Likewise, the curve for stainless iron with 0·09% of carbon stands above that for cutlery stainless steel with 0·27%; this agrees with the superior resistance to corrosion of the former material. Under comparable surface conditions, the homogeneous (austenitic) alloys yield higher curves than the duplex (hardenable) materials.

It is well known that a smooth or polished surface often remains passive where a rough surface is corroded. This is entirely in harmony with the exceptionally high value given by polished " Staybrite "—as compared with other surface treatments. Similarly, the curves yielded by electrolytic iron when prepared by abrasion on the wheel show a far more rapid descent than when prepared with French emery No. 1, whilst " Two-score " also gives lower values when prepared on the wheel alone than when afterwards finished with French emery No. 1. A comparison of Expts. 29—32 with 33—36 indicates that the latter finish develops a more resistant film than a wire-brushed surface.

A comparison of the potentials obtained with " Staybrite " after various preliminary treatments (Expts. 29—37) has some interest. Owing to the difficulty of reproducing " abrasive conditions " with this material, a 10 cm. square plate of the material was uniformly wire-brushed, and cut into four quarters, one being used in each of the four experiments 29—32; another sheet was subjected to the " sequence " of abrasive treatments, and its four quarters were used in Expts. 33—36. The curves obtained accorded generally with the known facts that (1) annealing at 500—900° lowers the resistance by causing the precipitation of a second phase, and possibly by producing a thick oxide film, which is visible, easily removed, and therefore non-protective; (2) pre-treatment with nitric acid raises the resistance of alloys of this class (Hatfield, *J. Iron Steel Inst.*, 1923, **108**, 123). It should be noticed, however, that the rise of potential after nitric acid treatment, although marked for " Staybrite " both on wire-brushed and " sequence-finished " specimens, is not obtained with stainless steel finished on the coarse wheel (Expts. 18—21). The unexpectedly high value found in Expt. 35 was probably due to the fact that the thick oxide film was very easily removed from the specimen, and left a surface much smoother than the originally abraded surface.

The curves obtained with aluminium all lie very close together, in spite of differences of purity and abrasion. Although there is a slight tendency to rise in the case of the less pure variety, all the curves are nearly horizontal, in contrast with those previously obtained with specimens placed vertically, which rose rapidly (J., 1929, 106). In the case of the latter specimens, the early attack was practically confined to the water-line and cut edges, and the aluminium hydroxide was evidently precipitated at the mouth of the pores in close contact with the metal, since it gave fine rings of interference colours; any hydroxide thus precipitated would tend to heal up the weak spots in the skin, accounting for the marked rise in potential. In the new experiments, where the water-line and cut edges are excluded, this action is evidently much slower, especially with the highly pure variety, and the potential is nearly constant.

Evidently the observed potential does not indicate the rate of corrosion; steel and aluminium give almost the same final potentials, and yet the steel is far more quickly corroded. When the shape of the potential–time curve is considered along with the "normal electrode potential" of the metal, however, the information obtained is consistent with the results of corrosion-velocity measurements and, indeed, more extensive. For steel shows at first a comparatively high value, which soon sinks to a value probably representing the potential of unprotected metal; but the potential measured for aluminium is always far above the theoretical value for this metal without a protective film, and tends to rise rather than fall with the time.

Composition of the Protective Oxide Film.—In previous work (Evans, J., 1927, 1020; Evans and Stockdale, J., 1929, 2651) it was shown definitely that the protective oxide film, *after* separation from passive iron, consisted of ferric oxide (or perhaps, in part, hydroxide) with some metallic inclusions. Bancroft, however, has written (private communication, July 3rd, 1927) that "electromotive-force measurements preclude the possibility of the film being Fe_2O_3. If one postulates that the film consists of an unstable, higher oxide, adsorbed by iron, the higher oxide would break down to Fe_2O_3 as soon as you dissolve off the stabilizing iron backing.' He urges that the film, as analysed, has not the composition of the film as actually present on the passive iron. Similar views have been expressed by Hale (*J. Physical Chem.*, 1929, **33**, 1637).

Undoubtedly, iron rendered passive by anodic treatment has at first a high potential, due to the oxygen supercharge, which *may* be present as an unstable higher oxide; but Smits ("Theory of Allotropy," p. 351, Longmans Green and Co., 1922) has found that, on standing, the potential sinks with a marked arrest at about + 0·54 volt (hydrogen scale); presumably, if the original high value is due to a higher oxide, the arrest represents ferric oxide. Since the iron is still passive during the arrest, it would seem that a higher oxide is not necessary for passivity.

However this may be, it is clear from Table I and Fig. 3 that iron rendered passive in potassium chromate never reaches the high potentials referred to by Bancroft. Indeed, higher values than this were obtained in some experiments where crystals of natural haematite or even magnetite were used instead of a metallic specimen. Not too much importance should be attached to these measurements, since the crystal could not be wholly immersed, and the measurements of the hæmatite varied from end to end, possibly owing to the zonal variation of oxygen content described by Sosman and Hostetter (*Trans. Amer. Inst. Min. Met. Eng.*, 1917, **58**, 409, 434). Actually the work of these authors, and also that of Smits and Bijvoet (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 386), Pfeil (*J. Iron and Steel Inst.*, 1929, **119**, 501), and others has shown that ferric oxide is merely a member of a range of solid solutions. Numerous observations make it doubtful whether the electrode potential can be used—as claimed by Bancroft—to estimate the oxygen content of a solid phase, and the method is particularly unsatisfactory when the phase is an oxide film backed by metal, which is probably not inaccessible to the liquid. But if Bancroft is justified in accepting the potential as evidence, it would seem that the oxide present on iron rendered passive by simple exposure to chromate or air has *not* a higher oxygen content than is represented by the formula Fe_2O_3.

Summary.

A new method has been worked out for obtaining potential–time curves, and has been applied in a study of the behaviour of iron, iron alloys and aluminium, after various abrasive, chemical and thermal treatments, in chloride and chromate solutions. The results given correspond to the behaviour of the film, a rising potential indicating that weak points are being repaired, and a falling potential that the breakdown is extending. A high final potential indicates immunity from attack, a middle value slight rusting, and a low value profuse rusting. Treatments known to increase the resistance to attack raise the potential, and those favouring corrosion lower the potential. The character of the curves probably indicates the "liability to corrosion" rather than the velocity of corrosion when fully developed, and gives information regarding the protective character of the skin, which velocity measurements cannot afford.

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