222. *Passivity of Metals. Part XII.* Intense Attack at the Water-line of Otherwise Passive Metal.*

By A. M. Peers and U. R. Evans.

Intense water-line attack occurs on iron partly immersed in sodium chloride solution containing phosphate, carbonate, or other anodic inhibitor in certain proportions. This has been studied (1) in presence of oxygen without applied current and (2) in absence of oxygen with applied anodic current. Water-line attack does not depend on special surface conditions, acid constituents in the air, or evaporation. It is greatly affected by the shape of the meniscus crevice, and by the presence of films. The results support Schikorr's suggestion that water-line attack is due to slow replenishment of inhibitor in the meniscus. It is thus a form of crevice corrosion—analogous to that produced at contact with a glass rod.

Water-line attack arises in many ways. That met with on metal partly immersed in acid (Evans, *J. Inst. Met.*, 1923, **30**, 272; Hedges, *J.*, 1926, 832) may perhaps be due to preferential renewal of oxygen or removal of hydrogen at the water-line. The breakdown of passivity at the water-line on iron in concentrated nitric acid may be due either to preferential escape of nitrogen oxides so that the ratio $H_2O : N_2O_5$ may here reach the activation range (Evans, *J.*, 1927, 1036), or to autocatalysis connected with the retention of reduction products at the meniscus crevice (cf. Evans, *Trans. Faraday Soc.*, 1944, **40**, 120). The water-line trenching of steel in hard waters may be due to the acid constituents of the air interfering with the chalky film which protects the immersed portions.

The present paper deals with the intense water-line attack of iron in liquids containing sufficient inhibitor to passivate the immersed area. It can be observed in dilute sodium carbonate (or bicarbonate) solution in the absence of chlorides, but is most intense in carbonate–chloride or phosphate–chloride mixtures. If iron plates are immersed vertically in sodium chloride containing carbonate or phosphate, the area suffering corrosion shrinks as the carbonate or phosphate content increases; the attack becomes localized and usually intensified; finally, at high inhibitor concentration, attack ceases. The localized attack sometimes occurs at sheared edges or at surface defects, but is particularly associated with (1) the water-line and (2) crevices formed where the metal is in contact with a non-conducting solid, *e.g.*, a glass rod. The water-line attack is often so intense as to cause perforation of a steel plate within a time when the more general corrosion set up by inhibitor-free chloride solutions produces only slight thinning (Evans, *J. Soc. Chem. Ind.*, 1925, **44**, 163; 1927, **46**, 347). The intensification is partly caused by the dangerous combination of large cathode and small anode, but in some cases the total corrosion (as opposed to the intensity of corrosion) is increased by addition of inhibitor in inadequate amount (Mears and Evans, *Trans. Faraday Soc.*, 1935, **31**, 527). The deep trench, formed along the water-line, is closed in by a rust-box of triangular cross-section, bounded above by a curved rust membrane clinging to the meniscus, and below by a wall of looser rust which roughly constitutes a prolongation to the level portion of the water surface.

In chloride solution free from added inhibitor, the (cathodic) water-line zone is protected, partly at least because the cathode product (sodium hydroxide) is itself an inhibitor. When the liquid contains an added inhibitor, there is no reason for special immunity at the water-line, but the preferential attack at that level, and also at crevices formed by contact with glass, still requires explanation. Two explanations deserve consideration, as follows.

(1) *Exhaustion Theory.*—Protective films are believed to develop discontinuities at intervals (Britton and Evans, *J.*, 1930, 1777; Evans, *Nature*, 1946, **157**, 732); unless the inhibitor supply is sufficient to repair these breaks as they occur, attack will develop; since the rate of replenishment of inhibitor will be less at the tip of a meniscus, or in any other crevice, than elsewhere, attack is most probable at such places.

(2) *Rival-interface Theory.*—Matter which, in the fully immersed portion, would be

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* Part XI, *J.*, 1952, 3432.

deposited on the metal and would serve to repair discontinuities, may be deposited, for reasons of surface energy, upon the air–liquid or glass–liquid interface.

Mears and Evans (*Trans. Faraday Soc.*, 1934, **30**, 417) compared these two theories by studying crevices produced at contacts between steel rods and glass rods. Movement of the liquid was found to *decrease* the frequency of local attack—which clearly favours the exhaustion theory. The attack was found to be *more* frequent at crevices formed between two steel rods than at crevices between steel and glass—which is difficult to explain on the rival-interface theory, since there is no obvious reason why " repairing matter " should desert one steel surface for another.

The rival-interface theory was retained for water-line attack, where the membrane clinging to the curved liquid–air interface appeared to provide ocular evidence. It was felt that if, at one point on the water-line, anodic attack set in, the good supply of oxygen at cathodic points close to it would provide conditions favourable for continued attack. Another possible cause of attack was, however, advanced by Thornhill (*J. Iron Steel Inst.*, 1942, **146**, 94P), who found that water condensing on the dry metal ran down and diluted the concentration of inhibitor at the water-line.

Schikorr (personal communication, *ca.* 1938) argued that the meniscus was merely a special type of crevice and that water-line attack was due to exhaustion of inhibitor. Now the main difficulty to all exhaustion theories is that, although a crevice undoubtedly interposes a " resistance " on diffusion paths leading to points situated within it, yet it interposes a similar resistance on the current paths connecting the points (as anodes) to some large cathodic area situated outside the crevice; whatever the geometry of the crevice, it should multiply both resistances by the same factor. Presumably the film will only be kept in repair if the maximum rate of replenishment of inhibitor exceeds the maximum rate of production of metallic ions possible in inhibitor-free liquid (both rates being expressed in equivalents per unit time). Hence *in the absence of complications*, the inhibitor-requirements will be reduced by the crevice in the same proportion as the inhibitor-supply, and the probability of attack in the crevice should be the same as elsewhere.

It seemed desirable to decide whether water-line and ordinary crevice corrosion are really the same phenomenon, to study the effect of varying the shapes of the " meniscus crevice," and to enquire whether the presence of films (as one of the " complications " mentioned above) can remove the objections to the " exhaustion " theory.

Specimens of iron were partly immersed in chloride–phosphate solutions of different compositions, special attention being given to the effect of (1) surface condition of the metal, (2) acid constituents in the air, (3) slow evaporation which might alter the meniscus shape, (4) composition of the solution, (5) vertical dimensions of the specimen, (6) time of immersion, and (7) shape of the " crevice." The measurements included : (*a*) the loss of weight, after removal of corrosion product; (*b*) the " incidence " (*i.e.*, the mean fraction of the water-line attacked as measured on all the specimens); (*c*) the probability of water-line attack (*e.g.*, the proportion of specimens which developed it); (*d*) the probability of attack elsewhere.

These experiments (Series I) required to be performed in multiple, since, in any phenomenon depending on a *small* number of events, reproducibility may be expected to be poor (Evans, " Introduction to Metallic Corrosion," Arnold, 1948, p. 174). Hence simple methods were adopted.

Interpretation of experiments under " natural " conditions (*i.e.*, without electric current applied from an external source) is difficult owing to doubts as to the position and extent of the cathodic area on specimens developing a meniscus box. In inhibitor-free chloride, the cathodic area is usually a strip 2 mm. broad at the water line and this simple geometry facilitates interpretation (Evans and Hoar, *Proc. Roy. Soc.*, 1932, *A*, **137**, 358). For inhibitor-containing solutions, simplicity may best be achieved by abolishing the cathodic area on the specimen altogether, using a solution and gas-space quite free from oxygen, and producing corrosion by means of an applied current, with a platinum wire as cathode. Such experiments (Series II) gave results useful in interpreting those of Series I. In Series II, the method was more complicated, and the number of experiments smaller.

EXPERIMENTAL

Material and Procedure.—The steel used was cold-rolled sheet 0·03 cm. thick containing C 0·26, Mn 0·36, Si 0·207, S 0·031, P 0·038%; the surface was bright and rust-free, defective portions being discarded. Unless otherwise stated, the word "specimen" means a piece 2 × 6 cm. with the longer side parallel to the rolling direction, and carrying a 3 mm.-diameter hole at one end. Specimens were usually hung from a glass rod as in Fig. 1, but in Series I(3), the float shown in Fig. 2, was employed. The work was carried out in a room kept by thermostat at 25° ± 1°. Where loss of weight was required, the corrosion product was removed by 10 seconds' immersion in 20% sulphuric acid containing 0·1% of di-*o*-tolylthiourea, followed by rinsing with hot water and immediate drying with a clean towel.

All reagents, including the benzene used for degreasing, were of analytical reagent quality. For degreasing, two sets of 10 specimens, previously rinsed in benzene, wiped, and weighed, were strung on nichrome wire each separated from its neighbour by a glass bead, and were extracted with benzene for 2 hours (Soxhlet), and hung to dry for 15 minutes at 110°. All glass vessels used were cleaned in potassium chromate and sulphuric acid.

Series I.—(1) *Effect of surface condition.* Sixteen specimens were subjected to each surface treatment. They were weighed and placed at an angle of about 30° to the vertical, each in a 60-ml. beaker containing 30 ml. of solution. The beakers were placed under a bell jar on a shallow tray and set aside for 2 weeks. The tray was kept filled with water to minimize evaporation losses. The solutions contained sodium chloride (always 0·017M) and disodium hydrogen phosphate of four concentrations (0·027, 0·034, 0·040, and 0·047M). Four specimens were tested in each mixture.

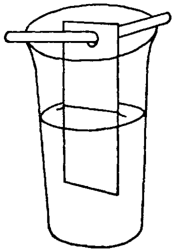


FIG. 1. *Partly immersed specimen.*

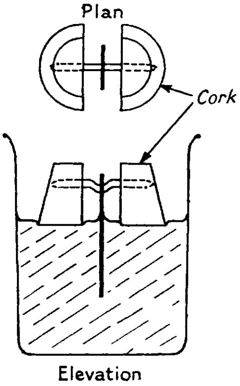


FIG. 2. *Buoy suspension, giving fixed water line.*

Each set of sixteen specimens received one of the following pre-treatments: (i) Wiping of the as-received surface with a dry cloth, to remove excess of oil used in packaging. (ii) Continuous washing with hot "AnalaR" benzene for 2 hours in a Soxhlet apparatus followed by 15 minutes' drying in air at 110°. (iii) Abrasion with "Oakeys" No. 1 cloth-backed emery. (iv) Abrasion with "Oakeys" No. 1 cloth-backed emery followed by benzene extraction as in (ii). (v) Rinsing in "AnalaR" benzene and annealing for 1 hour *in vacuo* at 950°.

After 2 weeks the specimens were freed from corrosion product and reweighed. The distribution of attack on each specimen was recorded. No serious differences were observed, although treatment (i) left a thin film of heavy oil on the specimen. Except for the most dilute concentration, the probability of water-line attack varied between 0·75 and 1·0, and the incidence between 0·4 and 0·6. The weight losses were least on specimens carrying oil films and greatest on annealed specimens.

(2) *Effect of acid constituents in the gas phase.* Ten specimens were cleaned with hot benzene, and tested when inclined at 30° in beakers, as already described. The solution contained sodium chloride (0·017M) and disodium hydrogen phosphate (0·040M). The beakers were placed in a large vacuum-desiccator containing concentrated potassium hydroxide solution. The desiccator was evacuated for 2 minutes with a rotary oil pump, then re-filled with air purified by passage through soda-lime, concentrated potassium hydroxide solution, and calcium chloride in that order. The above evacuation and re-filling was repeated three times.

After 2 weeks, every specimen had suffered attack at the water-line, the average incidence being 0·68. The results differed little from those obtained in the presence of unpurified air. Water-line attack cannot be attributed to atmospheric impurities.

(3) *Effect of slow evaporation.* Ten cleaned specimens were set up in 400-ml. beakers containing 225 ml. of solution of the composition stated above. Each specimen was suspended from a horizontal glass rod supported by a cork buoy which floated on the surface of the solution, as shown in Fig. 2. The buoys were coated with paraffin wax (previously purified by

FIG. 3. *Weight loss in* 0·017M-NaCl *containing* NaOH.

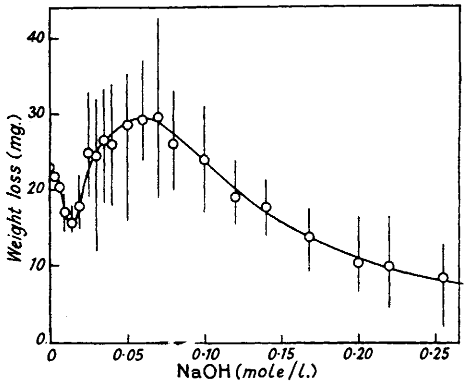


FIG. 4. *Weight loss in* 0·017M-NaCl *containing* Na_2CO_3.

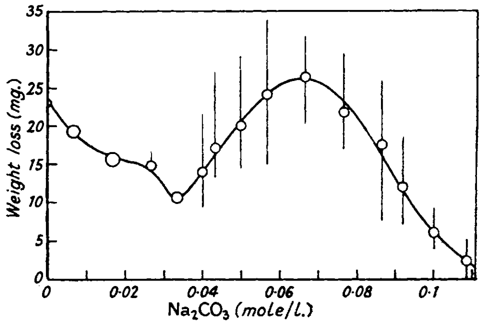


FIG. 5. *Weight loss in* 0·017M-NaCl *containing* Na_2HPO_4.

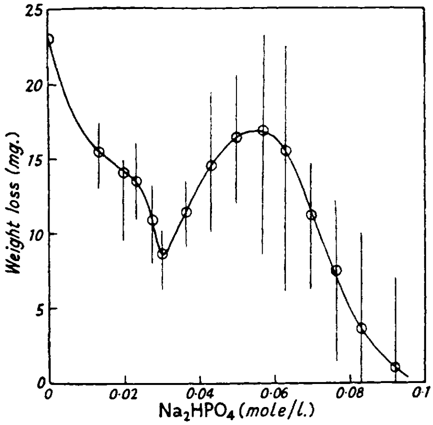


FIG. 6. *Weight loss in* 0·017M-NaCl *containing* K_2CrO_4.

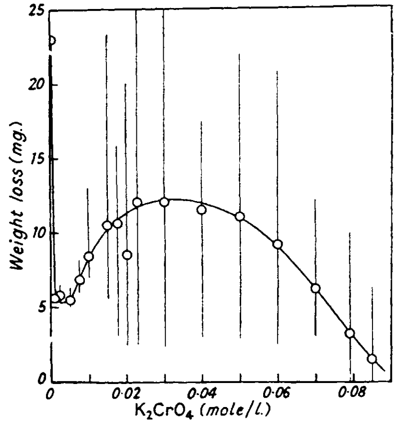
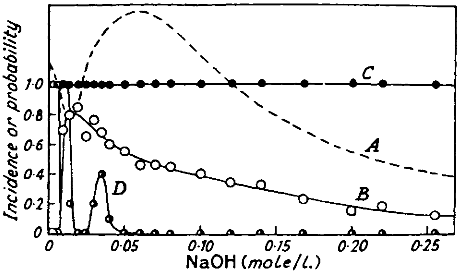
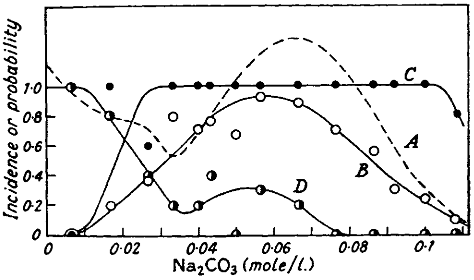


FIG. 7. *Water-line attack in* NaOH–NaCl *solutions.*



Curve A, weight loss (arbitrary ordinate).
B, " Incidence " of water-line attack.
C, " Probability " of water-line attack
D, " Probability " of attack elsewhere.

FIG. 8. *Water-line attack in* Na_2CO_3-NaCl *solutions (designation of curves as in Fig. 7).*



boiling with distilled water) to prevent the cork from absorbing water and sinking slightly during the experiment.

After 2 weeks, 8 specimens had suffered attack at the water-line. The average incidence (for 10 specimens) was 0·6. These results are not substantially different from those obtained in earlier experiments. Water-line attack cannot be attributed to slow evaporation.

(4) *Effect of composition of the solution.* Experiments were carried out on specimens immersed to a depth of 2·9 cm. for 168 hours. All solutions contained 0·017M-sodium chloride and varying quantities of an inhibitor (sodium hydroxide, sodium carbonate, disodium hydrogen phosphate, or potassium chromate). Figs. 3—6 show the variation of weight loss with composition; each point is the mean of ten experiments, the vertical lines indicating the scatter.

FIG. 9. *Water-line attack in* Na_2HPO_4–NaCl *solutions (designation of curves as in Fig.* 7).

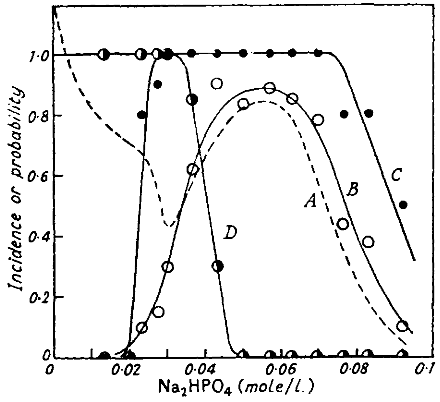


FIG. 10. *Water-line attack in* K_2CrO_4–NaCl *solutions (designation of curves as in Fig.* 7).

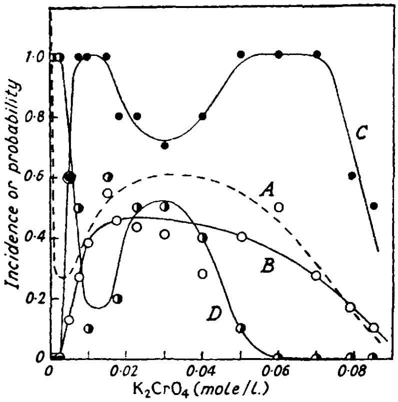


FIG. 11. *Dependence of weight loss on immersed length in* (1) NaCl *solution,* (2) NaCl–Na_2HPO_4 *solution.*

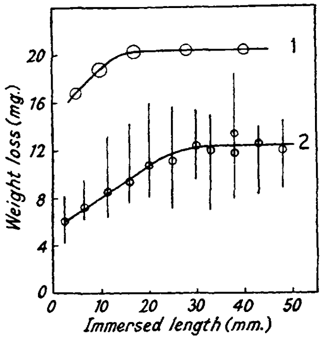
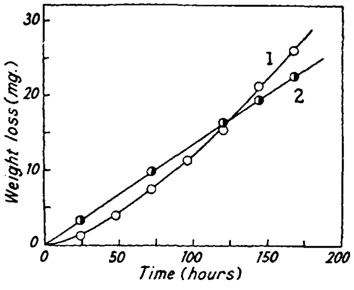


FIG. 12. *Dependence of weight loss on time in* (1) NaCl–Na_2CO_3 *solution,* (2) NaCl *solution.*



In Figs. 7—10, curve *A* shows weight loss (arbitrary ordinates), curve *B* incidence, curve *C* probability of water-line attack, and curve *D* probability of other attack.

Visible corrosion products generally appeared within 1—2 hours and, in almost all cases, were observed first at the meniscus head. At inhibitor concentrations just to the left of the weight-loss minima, before the incidence of water-line attack became appreciable, a neat double line of interference colours was often observed in the meniscus zone, indicating the growth of a visible film which was thickest along a horizontal line through the centre of the meniscus zone and tapered off towards the meniscus head and towards the meniscus foot.

(5) *Vertical dimensions of the specimen.* A large number of specimens were prepared as usual, except that the lengths were varied from 2·2 to 7·0 cm. The specimens were suspended vertically (as in Fig. 1) in 60-ml. beakers containing 41·5 ± 0·5 ml. of solution. The solution contained 0·017M-sodium chloride and 0·045M-disodium hydrogen phosphate. The length of the immersed section was measured from the meniscus head. The experiments were conducted under water-sealed bell jars for 7 days.

In Fig. 11, the average weight loss is plotted against the " immersed length," the distance between the meniscus head and the bottom of the specimen. On curve 2 each point represents the average weight loss for a set of ten specimens of a given length, the vertical line indicating the scatter. Curve 1 was obtained with 0·017M-sodium chloride solution containing no inhibitor. Each point on curve 1 represents the average of 5 specimens, the scatter being here shown by the diameter of the circles. The first point on curve 2 was obtained by adjusting the volume of the solution (within the limits 41·5 ± 0·5 ml.) until the surface of the liquid just touched the lower edge of the specimen; the recorded value (2·5 mm.) is the height of the meniscus.

(6) *Effect of time of immersion.* Seventy specimens were cleaned and vertically suspended in 60-ml. beakers containing 30 ml. of carbonate–chloride solution. The composition of the solution corresponded to the maximum weight-loss of Fig. 4 (0·017M-NaCl + 0·067M-Na_2CO_3). 25 Specimens were suspended under identical conditions in 0·017M-sodium chloride containing no inhibitor.

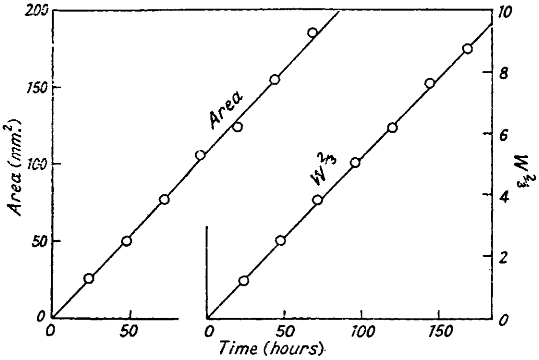


FIG. 13. *Linear dependence of area etched and (weight loss)$^{\frac{2}{3}}$ on time in* NaCl–Na_2CO_3 *solution.*

FIG. 14. *Device for controlling angle of inclination of the specimen.*

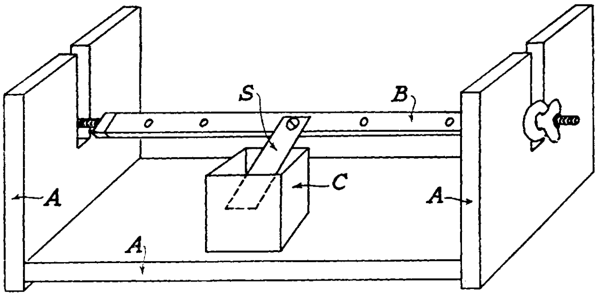
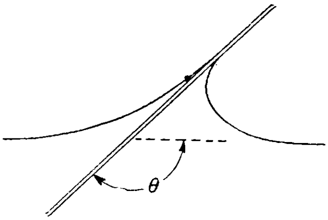


FIG. 15. *Schematic representation of dependence of dimensions of meniscus " crevice " on angle of inclination, θ.*



Each point on curve 1, Fig. 12, represents the average weight-loss for a set of 10 specimens in carbonate–chloride, and each point on curve 2 the average of 5 specimens in the chloride free from inhibitor. Curve 2 is rectilinear, in agreement with Evans and Hoar's results (*Proc. Roy. Soc.*, 1932, *A*, **137**, 343). In the carbonate–chloride solution, the variation in weight loss (W) with time (t) obeys the empirical equation $W = kt^{\frac{3}{2}}$, where k is a constant, as shown by Fig. 13.

The corroded area on each specimen, measured to within about ±1 mm.² by means of transparent graph paper, was found to increase linearly with time, as shown in Fig. 13; each point represents an average for 10 specimens.

(7) *Effect of shape of crevice.* Ten specimens were coated to within 3 cm. of the lower edge with a solution of paraffin wax in xylene. The film of paraffin, when dry, was thin enough to exhibit interference colours. The specimens were suspended vertically (as in Fig. 1) in 60-ml. beakers. 30 ± 1 Ml. of solution containing 0·017M-NaCl and 0·0435M-Na_2HPO_4 were added to each beaker until the meniscus was abolished by meeting the lower edge of the paraffin film (the liquid–solid contact angle now slightly exceeded 90°). Except for traces of corrosion product at the cut edges of two specimens, no visible attack was observed at the water-line in 7 days. Evidently, suppression of the meniscus crevice suppresses water-line attack.

Another arrangement (Fig. 14) permitted gradual variation of the angle. The frame *A*, was of thick aluminium sheet. The movable beam *B*, of insulating material, carried five holes and could be rotated to any desired position. The specimen *S* (2 × 7 cm.) was fixed to the beam by means of brass nuts and bolts. The solution was contained in a square vessel *C*, measuring approximately 4 × 4 × 4 cm., each containing 55 ml. of phosphate–chloride solution of the composition 0·017M-NaCl and 0·075M-Na_2HPO_4, which was chosen as representing a range where both the probability and incidence of attack at the water-line changed rapidly with the inhibitor-concentration (see Fig. 9). The length of the immersed section was set at 24 ± 2 mm. by vertical adjustment of the beam. Only one face of each specimen was exposed to the solution, the other being " masked " by application of polystyrene solution in xylene followed by paraffin wax.

Fig. 15 shows the relation between the angle of inclination of the specimen and the dimensions of the meniscus crevice, which becomes narrower as θ becomes smaller.

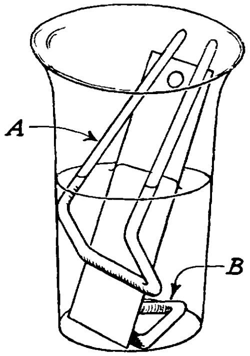


FIG. 16. *Arrangement of glass rods* (*A* and *B*) *for observing crevice corrosion.*

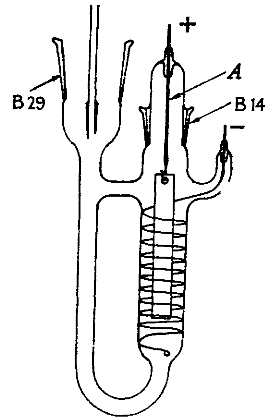


FIG. 17. *Cell B*1, *for observing distribution of anodic attack in oxygen-free solutions.*

The incidence and probability of attack at the water-line, after 7 days, are recorded in the following table: θ is the angle between the (exposed) surface of the specimen and the horizontal, measured through the liquid phase. Each value represents the average of 15 specimens.

Angle θ	30° *	60° *	90°	120° †	150° †
Incidence	0·71	0·52	0·35	0·27	0·26
Probability	0·73	0·53	0·40	0·30	0·30

* Upper face exposed. † Lower face exposed.

One early set of experiments gave different results. Square drops were obtained by placing liquid (0·017M-NaCl and 0·0435M-Na_2HPO_4) on a " chessboard " of waxed lines (Mears and Evans, *Trans. Faraday Soc.*, 1935, **31**, 527); by adjusting the volume of liquid applied to a square of fixed area, the apparent marginal angle could be controlled between wide limits. No significant variation of probability with angle was observed. The discrepancy is explained later.

The crevice corrosion obtained with glass rods (*A* and *B*, Fig. 16) was compared with water-line corrosion obtained as usual, 30 specimens being used. Observations supported the idea that the same mechanism is responsible for both phenomena.

Series II.—Method. The distribution of attack on mild-steel anodes partly immersed in oxygen-free solutions was observed after passage of a current of 12—13 μamp. on an immersed area 4 × 0·8 cm.(each side) for times varying from 13·6 to 120 hours. The anodes, measuring 0·8 × 6·0 cm., were individually annealed *in vacuo* for 1 hour at 950°. Where films of interference-tint thickness were desired, the annealed anodes were reduced in hydrogen at 750° and then exposed to purified oxygen at 225°. The procedure for annealing, reduction, and oxidation was similar to that of Gulbransen (*Trans. Electrochem. Soc.*, 1942, **81**, 327).

The Pyrex cell, *B*1 (Fig. 17) 1·8 cm. in diameter, was attached by a B 29 ground joint to the apparatus shown in Fig. 18 (in place of cell *B*). The anode was suspended from a hook of thick platinum wire attached with silver solder to the tungsten rod, *A*, which was sealed through the top of the B 14 joint. The electrical connection to the cathode also involved a vacuum-tight tungsten-Pyrex seal. The cathode was a platinum spiral which fitted snugly against the inner wall of the cell.

The solution (15 ml.) was freed from (and analysed for) oxygen in cell *A* (Fig. 18) by a method described by Peers (*Chem. and Ind.*, 1952, 969) and then transferred into cell B1 through the siphon tube, *C*. The small constant current was obtained from a 120-volt dry battery in series with a large resistance.

Results. In dilute sodium chloride containing no inhibitor apart from the alkali produced at the cathode (which caused the pH to rise from 6·5 to 9·5 where it remained stationary, the solubility product of ferrous hydroxide having been reached), the attack was general, provided the specimen carried only the film normally present after exposure to cold air. On tinted specimens, attack became increasingly *localized* at the meniscus as the film became thicker; for a given film thickness, the attack became less localized as the sodium chloride concentration was increased (Fig. 19). Specimens carrying only the low-temperature films suffered attack localized at the meniscus if phosphate was present. Thus water-line attack does not need the presence of oxygen.

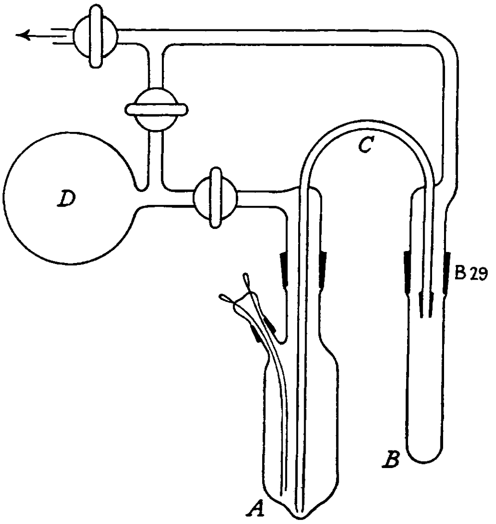
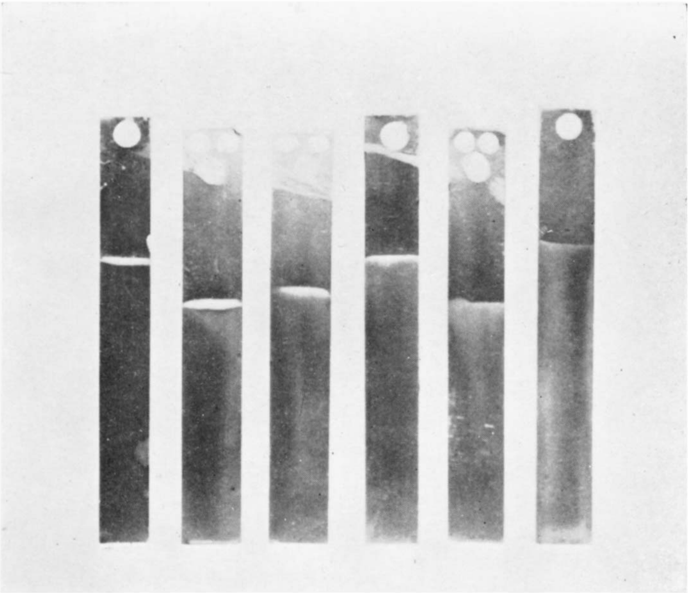


FIG. 18. *See text for explanation. Arrow leads to traps, gauges, gas purification trains, pumps, etc.*

DISCUSSION

Effect of Films.—The fact that carefully degreased specimens behave much like those not degreased shows that water-line attack is not due to removal of a protective grease film by cathodically produced alkali. A comparison between results obtained in closed and in open vessels, respectively, shows that it is not due to atmospheric acids causing passivity to breakdown locally. The experiments with external current in absence of oxygen show that oxygen is not needed, but that films are important. A specimen which has received no intentional oxidation suffers general attack in sodium chloride free from phosphate and oxygen; but if the specimen is superficially oxidized by heat-tinting, attack is largely confined to the water-line. If the liquid contains sodium phosphate, untinted specimens suffer attack confined to the water-line. Hence either a ready-formed film *or* a film-forming compound is necessary for water-line corrosion.

Corrosion of a film-covered specimen involves either (*a*) the outward movement of electrons through the (dry) oxide-lattice or (*b*) electrolytic migration through sub-microscopic pores which have become filled with liquid. Cationic movement through a lattice will be very slow at room temperature and is likely to be confined to weak spots (Hoar and Evans, *J. Electrochem. Soc.*, 1952, **99**, 212); these may be spots where discontinuities have recently occurred and have been incompletely healed, so that the film has not attained its full thickness. Electrolytic migration will also be limited by the



0·001 0·02 0·05 0·10 0·20 0·50

FIG. 19. *Dependence of distribution of anodic attack on chloride concentration. Anodes had been oxidized for* 20 *min. at* 225° *under* 12 *cm. of oxygen. Concn. of* NaCl *solution (moles/l.) is given beneath each anode.*

small combined cross-section of the pores. Thus the resistance to *cationic movement* imposed by the film is likely to be large—even though the film conducts electrons well. If we trace the current path between a small area on the metal situated within the crevice and a large cathodic area situated outside it (which may be part of the same specimen, as in natural corrosion, or may be an external platinum wire, as in the anodic experiments), the resistance of the part of the path where it crosses the solid film will be great compared to that of the part in the liquid filling the crevice. In other words, the resistance of a path approaching a small area situated within the crevice will not be appreciably higher than that of a path approaching a similar area outside the crevice; the current density (in absence of inhibitor) would be almost as great within the crevice as outside it, and the inhibitor requirements (for prevention of corrosion) will be almost the same at both places.

If the inhibitor could stop attack only by penetrating the film and reaching the metal, the crevice would have little effect on the replenishment rate compared with the hindrance imposed by the film. However, it seems likely that if inhibitor can reach the *outside* of the film in adequate quantity, it will serve to interact with cations which would otherwise emerge (whether through pores or through the lattice) and prevent them from entering the liquid. Mayne and Menter (unpublished work) find by electron diffraction that the film formed on iron immersed in sodium phosphate is largely γ-ferric oxide with considerable hydrated ferric oxide; the hydration and high oxidation-state suggest formation at the outside of the film. If so, the narrow path approaching a microscopic area within a crevice will impose a greater resistance to diffusion than the broad path approaching a similar area situated outside.

Thus, on a film-covered specimen, the inhibitor-requirements for points situated within a crevice are the same as for points situated outside, whereas the rate of replenishment of inhibitor is much lower within the crevice and the danger of attack there is much greater. This explains the setting up of attack at crevices (including meniscus-crevices), and the argument is equally correct whether the cathode is a platinum wire with externally applied E.M.F. or an area on the specimen itself which can be reached by dissolved oxygen. Hence, in presence of a film the objections to the " exhaustion " theory disappear. The general similarity established between corrosion at the meniscus and that at crevices formed by a glass rod, supports Schikorr's view that the same explanation applies to both.

Effect of Specimen Shape, Time of Immersion, and Liquid Composition.—The uncorroded area is greater on specimens partly immersed in chloride–phosphate (or chloride–carbonate) than in simple chloride solution. If the whole uncorroded area can act as cathode, and if the control is even partly cathodic, the *total* corrosion may be expected to be greater when inhibitor is present; Figs. 3 and 4 show this to be the case. Since the attack is concentrated on a narrow strip along the water-line, the *intensity* is *much* greater. The idea that control is partly cathodic accords with the increase in total corrosion when the immersed length of the specimen is increased (Fig. 11). In simple chloride solution, increase of this dimension (which would mainly increase the anodic area) has less effect on the rate of attack (cf. Evans, *J.*, 1929, **122**; Series *A*).

The assumption that the whole uncorroded area acts as cathode may seem to conflict with observations on phosphate-free potassium chloride, where the cathodic reaction was found to be confined to the meniscus zone; in this case, however, there was found to be no oxygen available for the cathodic reaction except at the water-line (Evans and Hoar, *Proc. Roy. Soc.*, 1932, *A*, **137**, 358).

However, the control cannot be wholly cathodic, since the corrosion-rate increases with time (Fig. 12), possibly owing to extension of the anodic area along the water-line in the manner described by Thornhill (*loc. cit.*). Whilst the anodic area is small compared with the cathodic area, a modicum of anodic control must be expected. When the anodic area has ceased to extend laterally (and, to some extent upwards), the velocity is not likely to increase further. Experiments in chloride–phosphate mixtures, lasting 64 days (Evans and Taylor, unpublished work), although showing poor reproducibility, give results suggesting a fairly constant velocity.

An unexpected feature of the curves is the wide range of inhibitor concentration over which water-line attack occurs.

Effect of Crevice Shape.—If water-line corrosion is a form of crevice corrosion, any geometrical alteration which broadens or narrows the crevice should diminish or increase the probability of water-line attack. The experiments with specimens waxed down to the water-line, so as to eliminate the meniscus crevice, showed no water-line attack—which accords with the argument. Those in which the angle was varied by tilting the specimens showed that probability increases as the crevice narrows—which also supports the theory. The square-drop experiments provided an apparent exception, since a reduction of the liquid volume in each drop—although narrowing the contact angle as viewed macroscopically—did not appreciably increase probability. These experiments were carried out before the curves of Fig. 9 were available, and unfortunately a composition was chosen corresponding to the centre of the probability-plateau; thus even though the alteration in the drop shape considerably affected the inhibitor supply, that would be unlikely to affect the probability of water-line attack. The square-drop method was not used again, being unsatisfactory in other ways for the purpose in question; the macroscopic angle may not represent the true angle and the wax may produce micro-crevices if depressions on the metal are bridged but not filled.

General Conclusion.—It appears that water-line corrosion and crevice corrosion are the same phenomenon, and that the attack is due to the inhibitor's being replenished more slowly in crevices than elsewhere, whilst the inhibitor requirements (for prevention of corrosion) are much the same as elsewhere, provided that a film or a film-forming substance is present. Schikorr's views receive general support, and the difficulties in accepting them—valid if films are absent—disappear when films are present. Slow replenishment of the inhibitor anion appears to be the most important factor causing crevice or water-line attack in solutions containing high concentrations of an anodic inhibitor. Nevertheless, the water-line attack produced on mild-steel anodes in mildly alkaline chloride solutions (pH 9·5), suggests that in certain circumstances the local increase in chloride concentration may be as important a cause of localized attack as the decrease in inhibitor anion concentration. One of us (A. M. P.) hopes later to discuss this in detail.

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