581. *The Pitting of Zinc by Distilled Water and Dilute Solutions.*

By U. R. Evans and D. E. Davies.

The object of the research was to explain the vertical arrangement of pits produced on zinc by distilled water, to study the corrosion products, and to explain their formation. The vertical alignment is due to corrosion product from an upper pit lodging at points below, and screening them from oxygen; lines of pits can also be set up by the screening action of a polythene thread. A zinc disc whirled in distilled water containing oxygen suffers no pitting. In stagnant water containing oxygen under high pressure, zinc remains unchanged; at ordinary pressure, it becomes pitted. The pits contain white matter and are surrounded by white rings (oriented zinc oxide and some β-hydroxide); further from the pits are films of interference-colour thickness (also oriented zinc oxide), whilst negatively charged colloid particles appear in the liquid. Salt solutions produce a distribution of attack different from that given by distilled water. The results are explained on the theory of oxidation and corrosion advanced by Hoar and Evans.

The attack produced by distilled water on zinc is slow, even in presence of oxygen; it is, however, localised as pits, and may cause perforation of thin sheet. Bengough and O. F. Hudson

(*J. Inst. Met.*, 1919, **21**, 59) noticed that on cast zinc placed in stagnant distilled water, the pits appeared in straight vertical lines. The arrangement was evidently connected with gravity; a disc of zinc immersed in distilled water contained in a slowly rotating beaker developed a pattern of pits recalling a Catherine wheel; centrifugal force here played the part of gravity.

Evans (*ibid.*, 1923, **30**, 257; *Ind. Eng. Chem.*, 1925, **17**, 363; *J.*, 1930, 486) obtained the same vertical arrangement of pits on rolled zinc. The distribution in distilled water was different from that obtained in sodium or potassium chloride solution. Drops of salt solution placed on a horizontal surface produced attack at their centres, with a broad unattacked zone around the periphery; a ring of zinc hydroxide was formed between the two zones. The results were explained on the basis of differential aeration. The alkali formed at the peripheral (cathodic) zone caused the liquid to spread, so that the area of the drops increased. Drops of distilled water produced attack close to their edges; the white corrosion product formed a crinkled ring which actually touched the periphery at some points, but at others was separated from it by a narrow area free from attack; the main attack occurred just within or below the white ring and, since no alkali was formed, there was no spreading. The presence of carbon dioxide was not needed for attack; water obtained by distillation of dilute sodium hydroxide solution and condensed directly as droplets on the zinc surface caused appreciable corrosion. If much carbon dioxide was present, the attack was considerable, but there was no white corrosion product. The effect of carbon dioxide on the action of distilled and natural water on zinc has been studied in detail by Kenworthy and Smith (*J. Inst. Met.*, 1944, **70**, 463).

E. A. Anderson and Fuller (*Metals and Alloys*, 1939, **10**, 282) found anhydrous oxide on zinc subjected to distilled water free from carbon dioxide, but basic carbonate where the water had contained carbon dioxide. Gilbert (*Sheet Metal Ind.*, 1948, **25**, 2003, 2243, 2441) reported hydroxide when London tap water acted on zinc. Feitknecht and Petermann (*Korrosion u. Metallschutz*, 1943, **19**, 181), studying the attack of zinc chloride solution on zinc, found considerable hydroxide (α-, β-, and ε-forms). In distilled water the inner film was oxide, and the outgrowth β-hydroxide. Feitknecht (private communication, December 21st, 1950) states that he would expect primary zinc oxide round the pits, and that the loose material covering the pits, although originally amorphous or α-hydroxide, might later change into oxide or β-hydroxide.

Not only is the distribution different for distilled water and salt solution, but also the kinetics. Bengough, Stuart, and Lee (*Proc. Roy. Soc.*, 1927, *A*, **116**, 449; 1928, *A*, **121**, 88; 1930, *A*, **127**, 42) showed that fairly concentrated potassium chloride solution attacks totally immersed zinc in presence of oxygen, according to a rectilinear law, the oxygen-uptake V, in time t, being given by $\mathrm{d}V/\mathrm{d}t = k_1$, whereas the attack by distilled water or very dilute potassium chloride solution was asymptotic, the relation being $\mathrm{d}V/\mathrm{d}t = k_2(V_\infty - V)$ where V_∞ is the limiting value of V and k_1, k_2 are constants. The rectilinear relation was found to be valid for alloys by Borgmann and Evans (*Trans. Electrochem. Soc.*, 1934, **65**, 249) who used cylindrical rods of zinc or alloy cast in glass. When corrosion was plotted against time, the points fell on straight lines, but the gradient varied. Thus spectroscopically pure zinc was attacked somewhat more slowly than " ordinary " zinc, whereas each alloy corroded at a different rate; iron and, still more so, copper increased the attack on " ordinary " zinc, whereas aluminium diminished it.

Bengough, Stuart, and Lee (*loc. cit.*) noticed that in distilled water and N/10,000-potassium carbonate the curves showed sudden breaks; after the corrosion rate had become negligibly slow, the attack suddenly started again, as though a protective film had disintegrated, and then gradually attack died down. Many such breaks on corrosion–time curves have been reported—for instance during the high-temperature oxidation of copper (Pilling and Bedworth, *J. Inst. Met.*, 1923, **29**, 529) and during the atmospheric attack on aluminium exposed to London air (Vernon, *Trans. Faraday Soc.*, 1927, **23**, 150).

The present paper describes an investigation into the causes of the localised attack, the vertical arrangement of pits, and the character of the corrosion products.

EXPERIMENTAL.

Zinc.—Two grades of zinc sheet (Zn/49, Zn/50) were kindly provided by the British Non-Ferrous Metals Research Association, and slabs of spectroscopically pure zinc by the New Jersey Zinc Company. The compositions are shown in the Table.

	Zn/49.	Zn/50.		Zn/49.	Zn/50.
Thickness	0·50 mm.	0·48 mm.	Cadmium, %...	0·002	Trace (<0·002)
Iron, %	0·002—0·003	0·002	Magnesium, %	Not detected	Trace (<0·001)
Lead, %	0·012—0·016	Trace (<0·002)	Tin, %	Not detected	Not detected
Copper, %	0·001	Trace (<0·001)	Aluminium, %	Not detected	Not detected

Many of the experiments were carried out on the " as-rolled " surface, after degreasing; the specimens were alternately immersed in acetone and withdrawn, the liquid film being sucked off with blotting paper before it could evaporate; they then received vapour-degreasing in benzene. In other cases the surfaces were abraded, after degreasing, by use in turn of Oakey's G,F,M,O, 2/0, 3/0, and 4/0, which leaves a very smooth surface; a further degreasing followed.

Both Zn/49 and Zn/50 gave practically the same types and distribution of pitting, and these were the same on a finely abraded as on an " as-rolled " surface. Commercial zinc sheet (" as-rolled " condition) gave somewhat similar pitting. The spectroscopically pure zinc, being rough, could only be used after abrasion, which may have introduced impurites; the same results were obtained.

Apparatus.—The distilled water used for the principal experiments was prepared in the laboratory by the further purification of " ordinary " distilled water, previously condensed in glass in a small laboratory still. Subsidiary experiments were carried out with samples of high-quality distilled water kindly provided by other laboratories. All samples gave similar results; the pitting produced by the purest water was more clear cut, the pits being deeper but less numerous than those produced by less pure samples.

FIG. 1.

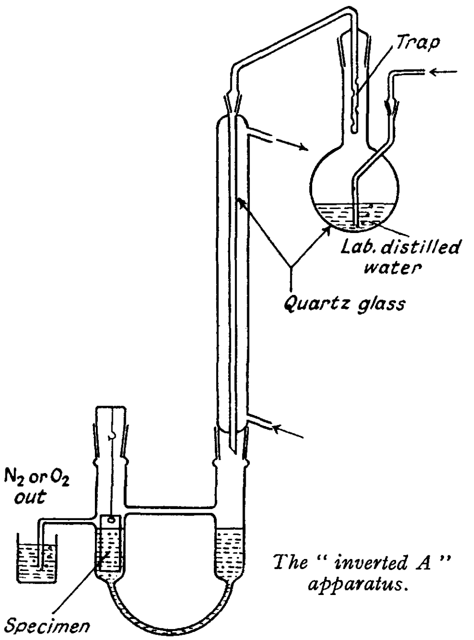
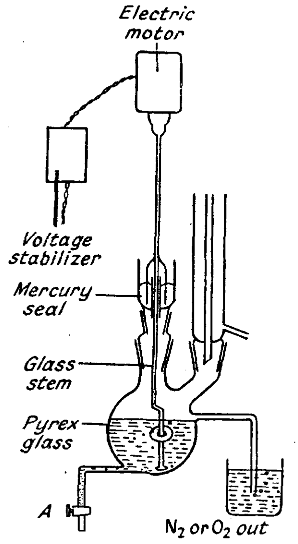


FIG. 2.



(*Not to scale.*)

In view of Kenworthy's demonstration of the effect of traces of copper salts on the corrosion of other materials (*J. Inst. Met.*, 1943, **69**, 67), metals were avoided in designing the still; the redistillation was carried out in an all-quartz apparatus, supplied by the Thermal Syndicate (Fig. 1), the design of the trap being due to Dr. A. E. J. Vickers, who kindly tested the carry-over. It was possible to pass nitrogen (purified by passage through 30% potassium hydroxide solution) through the boiling water, so as to wash out carbon dioxide, before condensation of the steam was started. It was also possible to attach, directly to the outlet, an " inverted A apparatus," which allowed the pH value to be obtained by means of a glass electrode, or alternatively allowed the action on zinc to be studied, without access of air. In general, the vessel was kept full of nitrogen whilst the inverted A apparatus was filling with water. No visible attack on the zinc occurred until oxygen was admitted.

The quartz-condensed water, if allowed exposure to the air, took up a pH of 5·3—5·5; this is close to the value 5·7 calculated for water standing in equilibrium with the amount of carbon dioxide commonly present in the atmosphere. When, by the nitrogen method, the carbon dioxide present in original distilled water was eliminated, a pH value as high as 8 was obtained, suggesting presence of a trace of ammonia. The conductivity varied between 0·07 and $0{\cdot}2 \times 10^{-6}$ mho cm.$^{-1}$.

Another method of obtaining pure water was to pass " ordinary " laboratory distilled water down a column of mixed resin " Bio-deminrolite F " which replaces the common anions by $(OH)'$ and the common cations by $H^{\cdot}$ (Akeroyd and Kressman, *Chem. Ind.*, 1950, 189); this gave a water of conductivity $0{\cdot}2 \times 10^{-6}$ mho cm.$^{-1}$ and pH 6·4—6·5. It is not clear how the pH numbers compare with those of samples prepared elsewhere, since most investigators have not quoted pH, but only conductivity.

When it was desired to whirl a disc of zinc under controlled conditions, the apparatus of Fig. 2 was employed (based on that of Evans, " Corrosion of Metals," 1926, p. 108, Arnold). The disc has a central hole large enough to fit loosely over the glass stem and when there is no rotation rests on the broad foot. During rotation it mounts up the stem, being in contact with glass at only one point at any moment; this point of contact is constantly changing, and there can be no screening from dissolved oxygen.

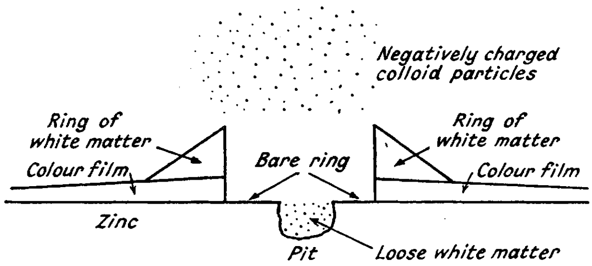
RESULTS.

Vertical Alignment of Pits.—Experiments on partly immersed vertical sheet specimens confirmed the arrangement of pits in vertical lines—somewhat " wavy " unless convection currents were eliminated (Fig. 3). The pits were filled with white corrosion product and were generally surrounded by rings of the white product; the rings around adjacent pits sometimes merged into loops. Outside the white rings, the zinc was unattacked but showed interference colours when viewed by specular reflection; the arrangement of the colours showed the film to be thickest nearest to the pits; contour traces obtained with a Talysurf apparatus appear to confirm this. When the rings of white matter were brushed off, the interference-colour film was found to continue below them (Fig. 4). *X*-Ray studies showed the white product scraped from around the pits to be zinc oxide with some β-zinc hydroxide (identified by a table of spacings kindly provided by Prof. Feitknecht). The white matter obtained from within the pits gave no lines—suggesting that it was amorphous, although the quantity was too small for confident decision. Electron-diffraction studies showed the material responsible for the interference colours to be the anhydrous oxide, with preferred orientation; the white rings also showed orientation. The original " as-rolled " surface was found to carry an anhydrous oxide film without preferred orientation, much thinner than the colour film, as judged from the feebleness of the rings.

After the experiment, the water contained colloidal particles, presumably zinc hydroxide, and gave a good Tyndall cone. Electrophoresis experiments showed that they carried a negative charge.

FIG. 4.

Highly diagrammatic.



In somewhat exceptional cases, the pits were found to follow marks left by the rolling, but in general they were independent of surface blemishes. The arrangement of pits along vertical lines was obtained on " as-rolled " or abraded specimens placed with the rolling or abrasion direction at 45° to the vertical. On hand-polished specimens, the pits were likewise arrayed vertically above one another; transverse abrasion lines made just before immersion remained free from pits. Evidently something dropping from the uppermost pits sets up pitting at points vertically below one another.

When zinc specimens were partly immersed in distilled water in a sloping position, the usual straight lines of pits and loops were obtained on the upper portion, where white matter produced by a pit situated at a high point could slide down the metallic surface until it lodged at some lower point, there producing a fresh pit. On the lower side, where solid matter breaking off from the surface must fall clear of the zinc, the tendency to the linear arrangement of pits was not observed.

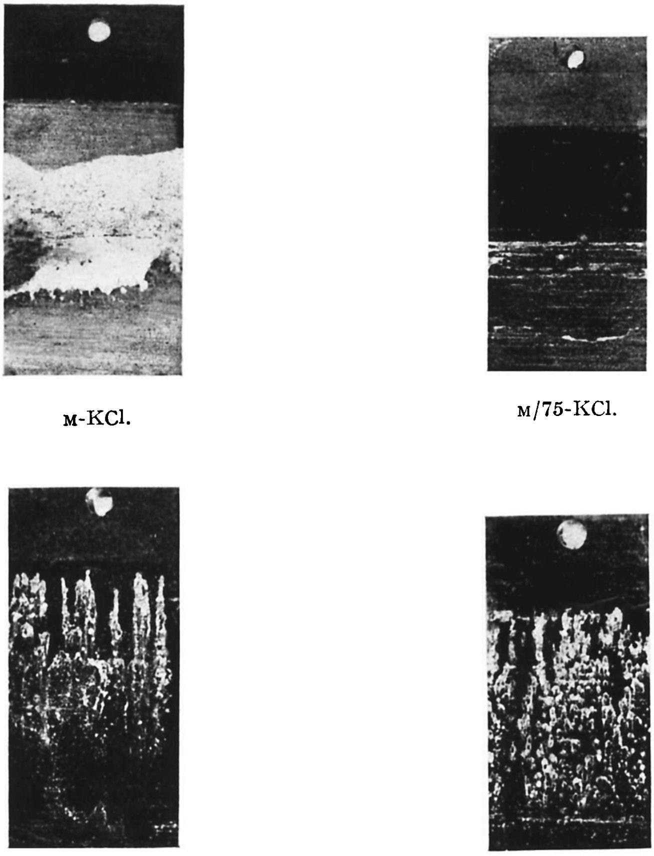
The distribution of attack was affected by impurities in the gas phase. Air purified by sodium hydroxide solution gave pits similar in some cases to those obtained with oxygen; if the purification was omitted, the corrosion extended over vertical streaks bounded by loops of solid white matter. There was then no pitting. This corrosion was probably due to the formation of appreciably soluble zinc hydrogen carbonate, and the phenomenon is probably analogous to the arch-shaped area of corrosion commonly noticed in the early stages when iron or zinc is immersed vertically in sodium or potassium chloride (Evans, *J.*, 1929, **117**; Borgmann and Evans, *Trans. Electrochem. Soc.*, 1934, **65**, 258). Along the edges of the arches are walls of membranous iron or zinc hydroxide formed by interaction between the iron or zinc chloride from within and the alkali formed outside.

Production of Pits by Contact with Other Materials.—If the white corrosion product from one pit can set up pitting at a point which otherwise would be immune, other substances might be expected to produce the same effect. Experiments were carried out on totally immersed horizontal specimens around which fibres had been tied or pressed. The fibres used included Polythene (drawn out in the laboratory to a fine thread), glass (similarly drawn out), and linen thread. The elastic character of the Polythene threads allowed them to be brought uniformly into contact with the metal surface over their whole length; thus they set up intense localised corrosion consisting of two parallel trenches or pit-lines, doubtless corresponding to the two crevices on each side of the line of contact (Fig. 5). The linen thread gave less pronounced trenching, whilst glass gave none. The materials may produce specific effects, but the effectiveness of Polythene is probably due to the formation of suitably shaped crevices.

FIG. 3.

Distilled water.

FIG. 7.



M-KCl.

M/75-KCl.

M/100-KCl.

M/500-KCl.

The most reasonable explanation of the intense corrosion at crevices (whether set up by corrosion product or by Polythene) is that the metal, being locally shielded from oxygen, becomes anodic to the main surface. The combination of small anode and large cathode leads, as usual, to intense attack.

Demonstration of the Corrosion Cell.—Since the idea of corrosion currents in liquids of poor conductivty is unfamiliar, it seemed well to study a "model cell" representing the situation at a pit. Helpful discussion with R. May, who has much experience of "model cells," led to the form shown in Fig. 6*a*; the liquid was distilled water. To break down the oxide already present on the lower zinc and thus start anodic attack, an electric current from an external battery was first passed under a current of nitrogen from the lower zinc sheet as anode to the upper zinc as cathode. When this external current was cut off by shifting the double-pole switch from the right-hand position to the left (Fig. 6*b*), the current started to flow back through *M*, with the lower zinc as cathode; this merely represented the usual behaviour of a polarised system, being analogous to the discharge of an accumulator. The back-flow current dropped to zero in about 3 hours, and in experiments under nitrogen no current was produced in the opposite direction. If, however, the nitrogen was replaced by oxygen soon after the polarising current had ceased to flow, then a current in the forward direction was obtained, the bottom zinc acting as anode and the upper (aerated) zinc as cathode. The current became constant after a few hours at a value varying in different experiments from 0·5 to 1·5 microamperes. The experiments suggest that a corrosion current can continue to flow through distilled water under geometrical conditions similar to those existing during the pitting of zinc.

FIG. 5.

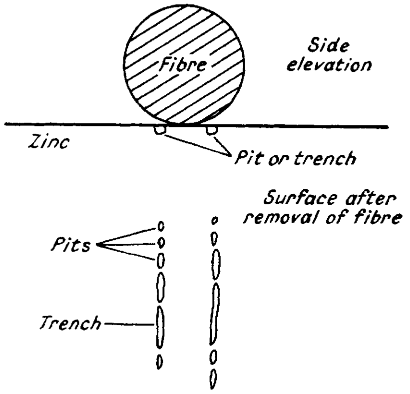
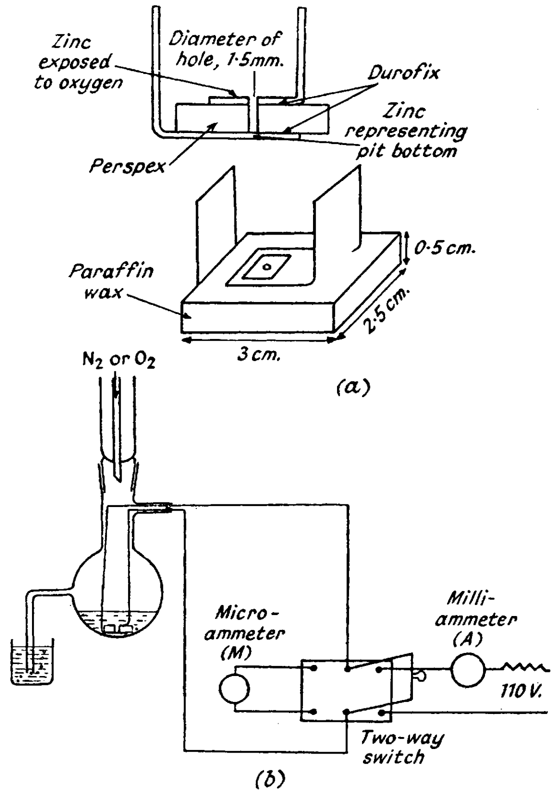


FIG. 6.



Experiments with Eccentric Whirler.—If the pitting or trenching set up by contact with zinc oxide particles (or with Polythene thread) is really due to local screening from oxygen, it would seem possible to prevent intense attack by maintaining an oxygen supply at all points on the surface, with the eccentric whirler (Fig. 2). A zinc disc whirled in distilled water with oxygen above the water surface remained free from pitting or any visible change; under stagnant conditions, experiments, carried out in the same apparatus containing the same water and the same oxygen, produced pitting, whether the zinc was totally or partly immersed. A small and rather variable concentration of zinc was detected in the water under whirling conditions, but this showed no tendency to increase beyond about 10^{-5} g.-ion/l.; the estimation was carried out in a Spekker apparatus by a method due to Mayne and Noordhof (unpublished work) based on sodium diethyldithiocarbamate. The loss of weight of the zinc at the end of 4 days was about 0·0008 g.—similar to that found in the water after whirling, namely 0·00065 g.

Experiments under Pressure.—Even under stagnant conditions, oxygen under pressure (10 atmospheres, decreasing to 7 atmospheres during the experiment) prevented pitting. This was shown by experiments in glass vessels enclosed in a stainless steel " bomb." Bengough and Wormwell's method (Report Chem. Res. Board 1935—1937, H.M.S.O., 1938, p. 17) was used, the high-pressure oxygen being introduced before the water; when the water was introduced before the pressure was raised, pitting occurred.

Experiments in Chloride Solutions of Different Concentrations.—Zinc was tested in potassium chloride solutions of concentrations 2·0, 1·0, 0·2, 0·1, 0·02, 0·01, 0·002, 0·001, 0·0002, 0·0001, 0·00002, and 0·00001M. In one series, plates were partly immersed in the solutions; in another, drops of solution were placed on horizontal plates. Well below 0·01M., the distribution somewhat recalled that produced by distilled water, with numerous pits surrounded by loops; at many points the corrosion product reached the water-line (in partial immersion experiments) or the drop margin (in drop experiments). Well above 0·01M., there was a continuous unattacked area below the water-line or around the drop periphery; this area showed high-order interference tints, indicating a film thickest near the water-line; electron diffraction identified the film as oriented zinc oxide. Round about 0·01M., both types of attack were found at different places. The situation is shown in Fig. 7. Sodium chloride and potassium sulphate gave similar results.

DISCUSSION.

Facts requiring Interpretation.—Any satisfactory mechanism must explain: (1) absence of attack when oxygen is absent; (2) pitting under stagnant conditions when oxygen is present; (3) absence of pitting under whirling conditions even though oxygen is present; (4) preferential pitting where particles of corrosion product settle or at contact with thread; (5) loose oxide and ε-hydroxide in pits; (6) negatively charged colloidal particles in liquid; (7) colour film of oriented zinc oxide thickening towards pits; and (8) white zinc oxide also oriented overlying colour film in its thickest region.

Effect of Oxygen Distribution.—The whirling experiments suggest that, to maintain a protective film on zinc, oxygen must be replenished as soon as it has been used up in repairing "weak points" of the film. When whirling stops, corrosion starts at certain points, although the oxygen concentration must at the moment of stoppage be uniform and equal to the saturation value. The weak points may be places where the film is rich in defects owing to the presence of impurities or broken by internal stresses; if the film has cracked at a point, it will during the repair process remain thinner there than elsewhere. The term " weak point " will include other places where the outward movement of zinc ions through the film is abnormally easy; for instance, places where the metal is disarrayed and thus energy-rich, providing a more rapid stream of cations through the film than occurs elsewhere.

Evidently there are grades of weakness. A very weak point will require a very rapid replenishment of oxygen for its effective repair. A moderately weak point may be repaired easily under the ordinary rate of replenishment characteristic of " unstirred " water, but not if that part of the surface is screened from oxygen by means of a Polythene thread. But shielding from oxygen, however complete, will not of necessity produce corrosion. All that it does is to increase the probability of corrosion; within a shielded region, there will in general be both pits and uncorroded zinc, although the shielding is, at the outset, no greater at the points which develop pits than elsewhere. The fact that the probability of attack increases as oxygen supply diminishes was shown for iron in distilled water by Mears and Evans (*Trans. Faraday Soc.*, 1935, **31**, 530).

If the pitting and trenching below a Polythene thread is attributable to oxygen-shielding, it is easy to explain the arrangement of pits on different surfaces. On a vertical surface, the corrosion product formed at a pit near the top will fall by gravity; if particles lodge at points on the surface, they will diminish the possible replenishment rate for oxygen so that minor weak points—which would not develop pitting on an unshielded surface—will become the sites of pits; hence the arrangement in vertical lines. This cannot happen on a horizontal surface; hence the original pits will not give birth to others. Nor can it happen on the lower side of a sloping plate; on the upper side particles can slide downwards and the lines of pits are again obtained.

Electrochemical Action around a Weak Point.—Imagine a horizontal zinc surface carrying an oxide film and placed in water containing dissolved oxygen; imagine that the main part of the film is sound but that one weak point exists, through which zinc cations can move outwards (also electrons, since the defects which permit movement of ions usually favour movement of electrons). If the rate of replenishment of oxygen in the liquid is good, there will always be a layer of absorbed oxygen *atoms* on the outer surface, which can be converted into *ions* by the electrons moving outwards; consequently the zinc cations as they arrive at the outer surface can take up their places between the oxygen anions, giving an extra layer of zinc oxide. Thus, the film locally thickens, by accretion on the outside—a mechanism precisely similar to that demonstrated by Wagner (*Z. physikal. Chem.*, 1933, *B*, **21**, 25) for the formation of oxide-films on *dry* metal; the thickening at the weak spot continues until the increased thickness reduces the rate of movement of cations outwards, in other words until the spot has ceased to be exceptionally weak; pitting is avoided.

If the liquid contains no oxygen, the emerging cations can enter the liquid, becoming hydrated. However, this would soon leave the metal negatively charged, and the escape of cations must then cease (except in so far as the charge can be balanced by the deposition of hydrogen ions at points around, which can probably be neglected owing to the high overpotential of zinc). Again, there is no pitting.

If the maximum rate at which oxygen can be replenished is insufficient to arrest the zinc ions as they emerge, but is sufficient to provide adsorbed oxygen atoms at the area of sound film surrounding, and *very* close to, the weak spot, then the excess of electrons left behind when the cations enter the liquid may serve for the reduction of the oxygen. In other words, electrochemical reactions are set up which may tentatively be written thus :

at the weak spot (anodic) $Zn = Zn^{++} + 2e$
on the sound film (cathodic) $O_2 + 2H^- + 2e = H_2O_2$

Since the number of cations produced is equal to the number destroyed, there are no unbalanced ions. The hydrogen peroxide could be reduced to water by further cathodic action, but since hydrogen peroxide has been detected in fairly large amounts in the action of distilled water on zinc or other metals (Traube, *Ber.*, 1882, **15**, 2441; Churchill, *Trans. Electrochem. Soc.*, 1939, **76**, 341; Delahay, *J. Electrochem. Soc.*, 1950, **97**, 198), the second step does not seem to be complete.

Once zinc cations have accumulated in the liquid and reached the cathodic area, a different cathodic reaction becomes possible. The adsorbed oxygen atoms are converted into ions by the electrons, and the zinc cations arriving from the anode take their places between them, giving fresh layers of zinc oxide, as identified by electron diffraction. This formation of zinc oxide differs from the ordinary oxidation in air in that cations arrive *from the outside*. Thus, provided that electrons can move easily through the film, there is no reason why the thickening rate should fall off with time. It now becomes apparent why the oxide film reaches interference colour thickness, which is not generally reached in ordinary oxidation processes except at elevated temperatures. Apparently the film resembles high-temperature oxide films in being under internal stress and breaks up when a certain critical thickness is reached (Evans, *Trans. Electrochem. Soc.*, 1947, **91**, 547), forming the loose white rings which overlie the colour films where they are thickest; the fact that the white matter of the rings shows the same preferred orientation as the colour rings indicates that it is formed by the break-up of the film and not dropped from the liquid.

When the liquid contains many zinc ions, they are presumably balanced by hydroxyl ions (the equivalent removal of hydrogen having taken place at the cathode). The solubility of zinc hydroxide (and oxide) is low, and sooner or later the liquid will become supersaturated. It has been shown by Aebi (Diss., Berne Univ., 1946, p. 10) that the least soluble (*i.e.*, most stable) of the possible phases is the ε-hydroxide, but that frequently a metastable phase is first deposited. Whichever compound is first precipitated, the particles, whilst still of colloidal size, apparently acquire a negative charge by adsorbing hydroxyl ions and thus become stabilised. They migrate by electrophoresis towards the anode and are presumably deposited; this may explain the loosely adherent white matter (probably amorphous) found in the pits.* It is only partially protective—as would be expected—but after a time the anodic attack is stifled, which explains the asymptotic corrosion-time curve established by Bengough, Stuart, and Lee (*loc. cit.*)—in contrast with the straight lines obtained in chloride solutions where both anodic and cathodic products are soluble, zinc hydroxide being formed when they meet. Thus the difference in the location of corrosion products, as well as in the character of the corrosion–time equation, is explained.

Electrochemical Action in Badly Conducting Liquids.—A necessary condition for electrochemical action in badly conducting solutions is that *very small* anodic areas shall be surrounded by annular cathodic areas; only in that case can a cathodic area (much larger than the anodic area) exist very close to the anode, keeping the electrolytic resistance small. In general, the

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* The white matter in the pits might also be due to anodic discharge of hydroxyl ions.

ratio of effective cathodic area to anodic area determines the intensity of attack, which explains the sharp pitting produced by distilled water (especially the purest distilled water) on zinc. In more concentrated (and better conducting) solutions the total corrosion is greater but the attack less intense. Any doubts about the possibility of a zinc–oxygen cell with distilled water as electrolyte are dispelled by the experiments with the model cell.

The explanation suggested for the behaviour of zinc in distilled water fits the general picture of corrosion and passivity put forward by Hoar and Evans (Electrochem. Soc. Spring Meeting, 1951). The same picture explains why alloying additions (*e.g.*, chromium and aluminium) which confer resistance to high-temperature oxidation also prevent wet corrosion. The mechanism now put forward for zinc has points in common with that suggested for tin by Brennert (Techn. Publ. Int. Tin Res. and Dev. Council, D. No. 2, 1935) and Hoar (*Trans. Faraday Soc.*, 1937, **33**, 1152).

Subsequent Breakdown of Films.—If the solid product formed both at cathodic and anodic areas is anhydrous zinc oxide, the system is metastable, since the ε-hydroxide is less soluble. If once a nucleus of hydroxide appears, presumably recrystallisation will quickly spread and the whole film may become non-protective. This may be the cause of the sudden recommencement of the corrosion of zinc in distilled water, after it has become very slow, as noted by Bengough, Stuart, and Lee (*loc. cit.*).

Concentration of Zinc reached in the Whirler Experiments.—According to Feitknecht and Häberli (*Helv. Chim. Acta*, 1950, **33**, 929) the solubility products $[Zn^{++}][(OH)^-]^2$ are as follows :

Amorphous $Zn(OH)_2$	$3{\cdot}9$—$5{\cdot}5 \times 10^{-16}$
α-$Zn(OH)_2$	$1{\cdot}4 \times 10^{-16}$ (Aebi, *loc. cit.*).
β_1-$Zn(OH)_2$ *	$5{\cdot}0$—$6{\cdot}0 \times 10^{-17}$

ε-$Zn(OH)_2$, the stable form, has naturally a still lower value; Feitknecht (private communication, July 28th, 1950) gives this as $2{\cdot}7 \times 10^{-17}$ if calculated on conventional principles, and $8{\cdot}4 \times 10^{-18}$ if the Debye–Hückel equation is used.† Aebi assigns to the anhydrous oxide a value 7×10^{-17}, corresponding to the equilibrium $ZnO \text{ (solid)} + H_2O \rightleftharpoons Zn^{++} + 2OH^-$. If 1×10^{-16} is taken as a basis of calculation and it is noted that the water assumes a pH value of 8·5 after the whirling experiment, or a pOH value of 5·5, then it is evident that, if the water becomes saturated with zinc oxide (or α-hydroxide), it should contain $10^{-[16-(2\times5\cdot5)]} = 10^{-5}$ g.-ion/l. of zinc, in agreement with experiment. If, however, the stable ε-hydroxide was being deposited, with a solubility product of about 10^{-17}, the agreement would be poor. Actually, since electron diffraction indicates the anhydrous oxide, the results are explained.

We thank Dr. J. W. Menter for fruitful co-operation in the electron-diffraction work, Dr. W. H. Taylor and Mr. G. J. Dickins for facilities in connection with the *X*-ray studies, and Prof. W. Feitknecht for valuable information regarding diffraction patterns of numerous compounds. One of us (D. E. D.) thanks the Department of Scientific and Industrial Research for a Maintenance Grant.

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* Feitknecht (*Helv. Chim. Acta*, 1949, **32**, 2294) states that the two forms of β-$Zn(OH)_2$ known as β_1 and β_2 give *X*-ray patterns differing only in intensity.

† The difference between the two values may cause surprise, and the reader is referred to the discussion of the matter by Feitknecht and Häberli (*Helv. Chim. Acta*, 1950, **33**, 922, especially pp. 930, 931). For the present purposes the question is not important, since no calculations in this paper are based on the solubility product of ε-hydroxide.