402. *The Electrochemistry of the Corrosion of Partly Immersed Zinc.*

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A new form of " dielectrode " has been designed for determining the distribution of cathodic and anodic areas on partly immersed metal. Zinc, if freshly washed with acid and immersed in N/1000-sodium chloride, suffers attack mainly along the " meniscus foot "; the meniscus zone remains immune from corrosion for at least two weeks—provided evaporation and disturbance be avoided. Electrical measurements show (*a*) that all places where corrosion can be observed to be occurring are definitely anodic, suggesting that corrosion is wholly electrochemical, (*b*) that the cathodic reaction occurs almost entirely at the meniscus head—the place to which oxygen, a stimulator of the cathodic reaction, can be supplied most readily. Places in the lower part of the specimen which escape serious corrosion are not cathodic but neutral.

Although in the present work the corrosion seems to be essentially connected with differential aeration currents, that should not be taken to mean that differential aeration is the sole cause of corrosion; many types of attack are known where this factor is entirely unimportant.

THE apparatus described recently (Thornhill and Evans, this vol., p. 614) for studying the corrosion currents around a scratch-line on iron is only adapted for corrosion by wet paper. An apparatus, based on a similar principle, has now been designed for specimens partly immersed in a dilute salt solution (the sensitivity falls as the solution becomes more concentrated). Whereas the previous apparatus detected currents flowing parallel to the surface, the new apparatus detects normally flowing currents, so that the direction of the deflexion at once distinguishes anodic from cathodic areas. The present paper is confined to a qualitative study of the distribution of anodic and cathodic areas on zinc, and their movement with time. The special object was to ascertain whether or not the visual observation of corrosion at different points corresponds to the electrical observation of anodic polarity. It is hoped to construct an apparatus for quantitative work later.

It has long been known that, when a zinc (or iron) sheet is partly immersed vertically in a chloride solution, attack is soon observed at numerous points distributed sporadically, and spreads out from some of these points, so as to produce corroding areas a short way below the water-line. Most of the points situated very near the water-line (except at the cut edges) heal up, so that an immune zone is formed along the water-line, with the attacked zone below it. The cause of water-line immunity is generally attributed to the fact that alkali, the cathodic product, is preferentially found in the zone where oxygen, the cathodic stimulator, can be renewed most readily. Thus, whereas the zinc salts formed by anodic action in the lower parts must travel a considerable distance before being precipitated as hydroxide, any zinc salts formed momentarily in the upper part are precipitated by the excess of alkali in physical contact with the metal, thus stifling any further anodic attack; it is well known that interference colours due to hydroxide films are visible in this region. These tints were originally regarded as due to oxide films (Evans, *Ind. Eng. Chem.*, 1925, **17**, 366) and later as due to hydroxide films (Fernsides, quoted by Evans, J., 1929, 111) produced through the agency of cathodically formed alkali. Bengough and Wormwell (*Proc. Roy. Soc.*, 1933, *A*, **140**, 402; *J. Soc. Chem. Ind.*, 1937, **56**, 352T) have found that neither on zinc nor on iron does water-line immunity persist indefinitely; after 72 days in N/2-sodium chloride, a zinc specimen suffered perforation at the water-line. Pitting along the water-line was later noticed by Borgmann and Evans (*Trans. Electrochem. Soc.*, 1934, **65**, 257); on sheet specimens it was much more marked in 2N- and N-potassium chloride than in N/10- and N/100-solutions—a matter deserving notice, since the present experiments were carried out at N/1000-concentration.

Owing to the curvature of the water surface, the term " water-line " is somewhat vague, and the terms " meniscus head," " meniscus zone," and " meniscus foot " will be used below (these terms are defined graphically at the right-hand bottom corner of Fig. 2, p. 2113). Since, on etched zinc, the alkali formed in the meniscus zone creeps up the previously dry portion (forming a damp " creep-zone "), the meniscus head ultimately becomes less sharply defined than the meniscus foot, but is taken as 2 mm. above the latter.

Preparation of Specimens.—The zinc sheet used was 0·4 mm. thick and contained 0·01% Cu, 0·01—0·02% Pb, 0·005% Fe, 0·007% Cd, and a trace of silver. Our thanks are due to Dr. Moore and Dr. Brownsdon for the presentation and rolling of this material. It was abraded with Hubert emery paper No. 3, and cut into specimens 2 × 2 cm., which were washed with acetone, stored in a desiccator for over a week, mounted on celluloid, which was subsequently waxed as described elsewhere (*Chem. and Ind.*, 1938, 593), and replaced in the desiccator for one day. The surface was etched just before use with N-sulphuric acid for 3 minutes, then washed with water and dried. The acid etching was necessary to remove the oxide film. If it was omitted, the corrosion (in the dilute solution employed) was slight, localised, and irreproducible in distribution.

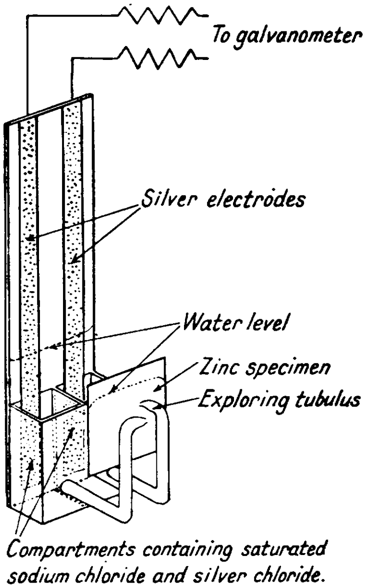
The steel used in certain subsidiary experiments contained 0·115% C, 0·045% Si, 0·020% S, 0·072% P, 0·350% Mn, 0·050% Cr, and a trace of nickel; this was abraded, but not etched with acid.

Experiments without Electrical Measurements.—Twelve specimens of zinc, etched as above, were allowed to corrode in N/1000-sodium chloride in the cells described elsewhere (*ibid.*), which permit access of air without evaporation of liquid. The cells were placed in a thermostat at

25·0°, and were dismantled—one at a time—after periods of 1, 2, 4, 8, 16, 32, and 44 days severally. The sequence of specimens thus obtained constituted a narrative of events. In the early stages, the specimens showed a white line at, or just below, the meniscus foot, which gradually passed into definite pits covered with loose white matter; the meniscus zone itself was quite unattacked. On the 32-day specimen the attack was still strongest close to the meniscus foot, but it had begun to extend further down; the meniscus zone was here completely immune, in contrast to the creep zone which was slightly darkened. On the 44-day specimen the immune zone was present, but was interrupted by microscopic etched streaks (actually, their commencement could be observed in the 16-day specimen). During the later stages the usual white mantle was observed growing out at right angles to the metal along the boundary of corroded and uncorroded zones. These experiments proved that: (1) *The appearance of adherent white matter can be taken as the first sign of corrosion occurring on the site in question* (this is not self-evident, since zinc hydroxide might be formed from the products of corrosion occurring elsewhere; in fact, non-adherent gelatinous hydroxide, which did not indicate the presence of corrosion at the point where it happened to be resting, was often encountered). (2) Under stagnant, thermostatic conditions, the distribution of attack on acid-washed specimens shows a satisfactory reproducibility.

A few experiments were carried out with zinc not washed with acid. Eight specimens were abraded with Hubert emery paper No. 3 and washed with acetone; four were introduced into N/1000-sodium chloride 5 minutes after preparation, and others were kept in a desiccator for 10 days before the experiment. On the first day the freshly abraded specimens showed temporary breakdown at the meniscus head, which, however, soon ceased to develop; this early water-line attack was absent on the specimens pre-exposed to air for ten days, although these showed water-line breakdown after 3 days. After 82 days there was no very marked difference between the two sets; corrosion was irregular, and, being still localised in patches, was somewhat intense. The specimens still showed an extensive but interrupted unattacked zone below the water-line, in some cases extending several mm. below the meniscus foot, with intense corrosion at the lower boundary of this immune area; on five specimens the corroded area extended up to the meniscus head at points. A corresponding set of mild-steel specimens showed no localisation of attack; the corroded area covered the greater part of the specimen and at points reached the meniscus head; the immune zone extended a few mm. downwards from the water-line with interruptions in places.

FIG. 1.



Other experiments were conducted on six similar specimens of zinc not washed in acid, corroded in N/2-sodium chloride solution. Three of the vessels were tipped up slightly once a day so as to wet the zinc above the water-line; the others were left undisturbed. The specimens in the first case showed water-line breakdown after 20 days, but the others did not show it until 70 days; on one of these, the water-line was still immune after 80 days. An analogous set of steel specimens in N/2-sodium chloride still showed a large immune zone just below the water-line after 80 days, whether tipped or not.

Electrical Apparatus.—The new form of "dielectrode" (Fig. 1) consists of two silver/silver chloride half-cells side by side, enclosed in a waxed celluloid frame, and attached to a celluloid strip, up which the two silver electrodes extend, making contact at the top with flexible wires leading to a Weston galvanometer (1 division = 25 × 10^{-8} amp.). The celluloid strip is attached to the supporting stand by a triple-screw arrangement, similar to that described elsewhere (*ibid.*) but permitting slow travel in *three* (instead of two) directions at right angles. The half-cells contain saturated sodium chloride, with solid sodium chloride present, and a few drops of silver nitrate are added just before sealing. From each half-cell extends a bent glass tubulus drawn out to a blunt point 1 mm. in internal diameter. When moved forward so that the end of one tubulus just touches the zinc surface, the end of the other is 8 mm. distant. A needle pointer attached to the travelling parts moves over a scale of squared paper, and enables the exact position where the tubulus will touch the zinc to be adjusted before the movement at right angles to the zinc surface is commenced; the slowness of travel minimises stirring and disturbance of corrosion products. All solutions must be boiled before the experiment; otherwise, bubbles appear in the tubuli and add greatly to the resistance.

The zinc specimens are fixed in a waxed celluloid trough with a glass front, and, after being washed with acid, are immersed to a depth of 1·2 cm. in freshly boiled N/1000-sodium chloride. The trough is covered with a lid, and, although a slit must be provided for the movement of the strip supporting the dielectrode, a second lid attached to the latter enables the vessel to be completely enclosed when not in use.

When the dielectrode is far from any corroding surface, the element

$$\mathrm{Ag}\left|\begin{matrix}\text{Satd. NaCl}\\ \text{Satd. AgCl}\end{matrix}\right|\text{N/1000-NaCl}\left|\begin{matrix}\text{Satd. NaCl}\\ \text{Satd. AgCl}\end{matrix}\right|\mathrm{Ag}$$

being symmetrical, can furnish no current. When one tubulus is brought into contact with a corroding surface, the difference of potential between the mouths of the tubuli destroys the symmetry, and a current is registered, the direction of which indicates whether it is in contact with an anodic or a cathodic area (a fact verified by using the apparatus on a compound specimen consisting of copper and iron). The proportion of current diverted through the galvanometer will be greatest when the liquid in the trough is dilute and that in the dielectrode concentrated; hence the choice of concentrations indicated above. Provided that the end is not in contact with a point-anode or point-cathode, or with the creep zone, the deflexion will be approximately proportional to the local magnitude of the current density. If current flow were exclusively normal to the surface, it would be possible to calibrate in a cell fed with known currents and then to determine the absolute strength of the current density at any position on a corroding specimen, without the differentiation process needed in the case of the earlier apparatus (Evans, *Nature*, 1935, **136**, 792). Actually, however, corrosion currents often tend to diverge from (or converge upon) " point-anodes " or " point-cathodes," and at such places the reading would be too low, whilst, on the " creep zone " above the water-line, it would be too high.

Another cause of inaccuracy is the local rise in concentration due to diffusion from the tubuli; for both these reasons the present results must be regarded as qualitative.

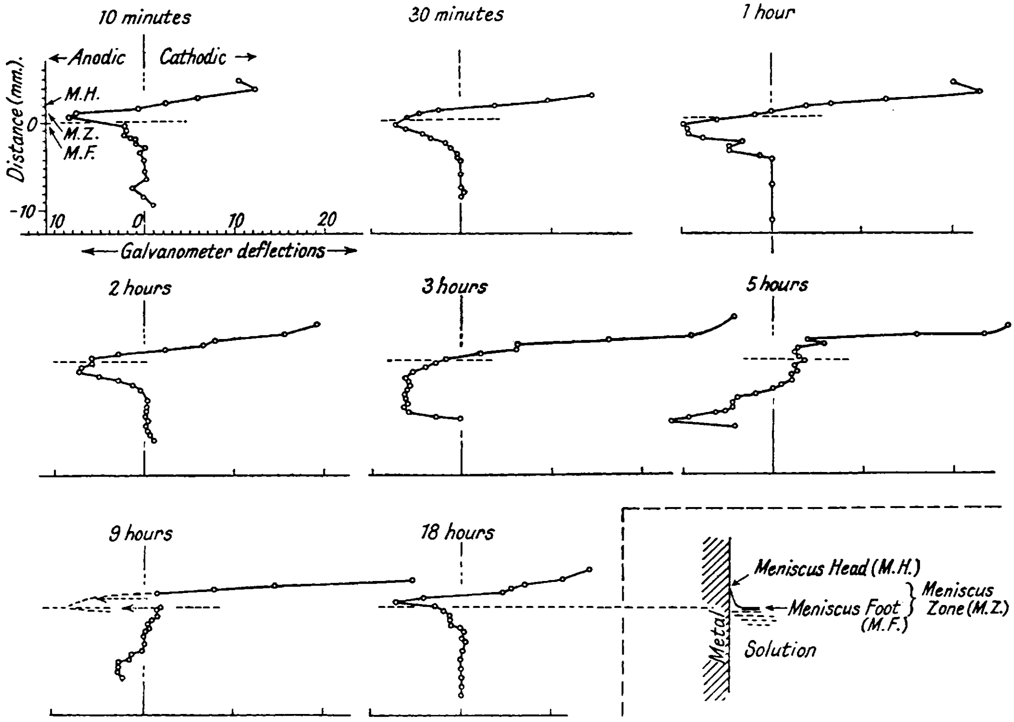
Altogether 10,000 electrical readings were taken; as the observations were mutually consistent, the results can be summarised briefly.

Experiments with a Series of Specimens undisturbed until the Time of Reading.—A large number of specimens were partly immersed in the solution, and left undisturbed until the moment arrived for an electrical survey. By carrying out surveys on different specimens after different periods of immersion, a complete electrical narrative was constructed. The usual procedure was to bring the exploring tubulus opposite a point on the lower edge of the zinc specimen (about 1 cm. away), then to screw it inwards until it touched the surface, take a reading, and screw it away again; the procedure was repeated at numerous points (0·5 mm. apart) on the vertical line above the original point. Typical examples of the distributions after different periods are shown in Fig. 2, where readings to the right represent cathodic currents, and those to the left anodic currents. The distribution beyond 18 hours is not shown as it remained practically the same for several days.

In all experiments where the portion above the water-line was not intentionally wetted before the experiment started, the main cathodic area was found close to the meniscus head throughout the whole experimental period (16 days); this area remained quite uncorroded. The main anodic area was at first at the meniscus foot, then after about 3 hours it passed lower down, usually reaching the bottom of the specimen after about 5 hours, and then returned after about 18 hours to the meniscus foot, where it remained for several days. Anodic readings continued at the meniscus foot throughout the period, but the maximum reading was about 1 mm. below the foot after 8 days and 2 mm. below it after 16 days. The persistently anodic zone just below the meniscus foot corresponded to the line of intense corrosion already mentioned, whilst the tendency for the maximum reading to descend corresponded with the movement of the etched area downwards; the places near the bottom of the specimen, which became temporarily anodic between the 3rd and the 18th hour of the first day, developed white matter during that short period, but corrosion ceased to develop at these places when the anodic area had returned to near the meniscus foot. *The close correspondence between the electrically-observed anodic areas and the visually observed attack suggests that the corrosion is wholly electrochemical.*

In all experiments, the main cathodic area lay above the main anodic area. Much of the lower part of the specimen suffered little or no attack; electrical measurements, however, showed these areas to be not cathodic but neutral. Specimens which were wetted before the experiment above the water-line by means of a strip of filter-paper developed a cathodic area on the wetted zone; the anodic area then occurred where the meniscus head would otherwise have been.

FIG. 2.



The distribution of cathodic and anodic areas appears to be determined mainly by differential aeration. On the specimens not wetted above the water-line before the experiment, the cathodic area is at the meniscus head—the only place which oxygen can reach without passing through a sensible thickness of liquid. The surface layer of any liquid forms a barrier through which only the most rapidly moving molecules can pass; according to Miyamoto and Kaya (*Bull. Chem. Soc. Japan*, 1930, **5**, 135), a water surface at 25° admits only one in 6,000,000 impinging molecules of oxygen. Many physicists consider that the surface layer of a liquid possesses an orientated quasi-crystalline character, but probably the orientation will become confused where the three phases, metal, liquid, and gas, come together, facilitating the passage of gaseous molecules. This fully explains why the cathodic reaction is largely concentrated at the meniscus head.

For the anodic attack, two sets of points will compete : (*a*) those situated along the meniscus foot, the region nearest to the main cathode (within the meniscus zone itself the supply of alkali is likely to be too high for anodic attack to develop), and (*b*) any points lower down where the physical structure is sufficiently loose to shift the potential in the anodic direction.

The electrolytic resistance of a path joining the (*b*) points to the main cathode will be somewhat higher than that of the path joining the (*a*) points, but this may be compensated for by the higher *E.M.F.* given by the (*b*) points. It is well known that attack at such areas requires a little time for this development, since the removal of the first atoms in the loose structure will facilitate the removal of other atoms around them. Thus it is easy to understand that, at the outset, most of the anodic attack will be directed upon the meniscus foot; later it will be directed mainly on any physically loose areas in the lower part of the specimen, and finally, when the supply of unstable matter on these areas has been exhausted, it will return to the meniscus foot, and remain in that neighbourhood indefinitely, thus minimising the resistance of the cell.

Clearly, the period during which attack will continue on the lower portions of the specimen will depend on the quantity of disorganised matter remaining, but may also be affected by the conductivity of the liquid; high conductivity will favour attack at a distance from the cathode. Thus in the experiments on specimens not washed with acid, marked corrosion on the lower regions continuing for several days was noted, especially those conducted in the more concentrated (N/2) solution.

Experiments with a Succession of Readings made on a Single Specimen.—In certain early experiments, readings were taken at different times on the same specimen, frequently four different vertical lines being explored. It was found that the movement of the tubulus to the surface modified the subsequent distribution of attack, and such experiments do not show the electrical history of an undisturbed specimen. Nevertheless, these experiments gave one instructive result.

When the tubulus was moved upwards over the cathodic zone at the meniscus, carrying up water and rendering the zone above definitely wet, then the part above the meniscus became cathodic, and the meniscus zone itself became anodic, as was shown both electrically and by the appearance of local water-line attack. Although this type of water-line attack is due to disturbances (either the wetting of the metal above the meniscus or the increase of sodium chloride concentration within the meniscus), the electrical observation may subsequently prove helpful in explaining certain cases of naturally occurring attack at the meniscus head. The fact that, even after the initiation of water-line attack, the cathode remains above the anode, suggests that, in certain cases described in previous work, where early water-line immunity is replaced later by water-line attack, the two stages may have been *merely two different aspects of the same phenomenon*, the only difference being that the level of the line separating anodic and cathodic areas has moved slightly upwards. This is certainly not the explanation of all types of water-line attack, which are clearly diverse in character (Evans, *Chem. and Ind.*, 1936, 210).

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