231. *Some Aspects of the Modern Theories of Corrosion. Part II. The Distribution of Corrosion.*

By J. E. O. Mayne.

In Part I (this vol., p. 366) reference was made to the work of Evans and his co-workers on the distribution of corrosion on steel plates partly immersed in *N*/10-potassium chloride solution. In the absence of convection currents and vibration, the distribution which they have established is shown in Fig. 1(*A*). Evans and Hoar (*Proc. Roy. Soc.*, **1932**, *A*, **137**, 343) state that the corrosion along the vertical edges of the specimen is " due to the descent of corrosion products from weak points situated on the cut edges, the products cutting off oxygen from the metal thus blanketed." On the other hand, Bengough (*J. Soc. Chem. Ind.*, **1933**, **52**, 238) states that " the special tendency of the edges to corrode is no doubt due to the difficulty of making the edges of emery-ground specimens exactly like the faces."

Experimental.

In order to test these explanations, the vertical edges of a small piece of steel 5 × 8 × 0·3 cm. were carefully rounded and polished, until the surface was the same all over. The specimen was then degreased, and partly immersed in *N*/10-potassium chloride in air in a thermostat maintained at 25°. After 3 days corrosion had taken place in accordance with Evans's " ideal distribution " as shown in Fig. 1(*A*). It does not appear, therefore, that this type of corrosion is due to the cut edges.

A careful examination of the work of Evans, Bengough, and their respective co-workers on partly immersed specimens revealed the fact that all their experiments had been performed on steel specimens in the form of thin plates, *i.e.*, specimens of which the width was very much greater than the thickness.

Four steel specimens, all 3″ × 1″ in two dimensions, but severally ¼″, ½″, ¾″, and 1″ in the third, were polished with No. 1 emery, degreased in carbon tetrachloride, and partly immersed as before in $N/10$-potassium chloride solution. After 3 days the distribution of corrosion was found to be as in Fig. 2, from which it can be seen that the corrosion along the vertical edges of the specimen is a function of its shape, in that, when the specimen is square, no preferential corrosion takes place at the edges. A possible explanation of this is that the distribution of corrosion is governed by the distribution of alkali over the surface of the specimen. Thus, if the alkali is formed near the surface of the solution, its movement will be governed by two factors: (1) It will tend to move down the surface of the specimen by the action of gravity. Evans and Hoar (*loc. cit.*) have shown that this is so, and have suggested that it is dragged down by the sinking of the ferrous chloride formed on the lower part of the specimen. (2) Owing to the high mobility of the hydroxyl ion it will tend to diffuse out into the solution in all directions.

Now, if the protection observed is due to the presence of alkali, then on a thin specimen, where only the front face has to be considered, the action of these two factors will give rise to Evans's ideal distribution. As the thickness of the specimen increases, however, the corrosion on the front face will be influenced by the facts that: (1) As the alkali diffuses away from the vertical edges of specimen, it will be reinforced by alkali diffusing in from the surfaces of the specimen at right angles. (2) Since the oxygen supply does not increase as rapidly as the metal–liquid–air interface, the concentration of the alkali per unit length of the interface will be lower. Thus the action of these two factors will destroy the ideal distribution, and the protected area will become narrower but extend evenly round the specimen.

In order to examine the effect of alkali distribution, experiments were performed in an air thermostat maintained at 25° on steel plates, partly immersed at an angle of 45° in $N/10$-potassium chloride solution. The vessels used in the following experiments were rectangular troughs 4″ × 3″ × 3″, which were covered by a bell-jar. It was found, however, that after 3 days under these conditions the distribution of corrosion on a steel specimen followed Evans's ideal distribution, although the corrosion on the upper side [see Fig. 1(*B*)] appeared to be much greater than on the lower [see Fig. 1(*C*)].

FIG. 1.

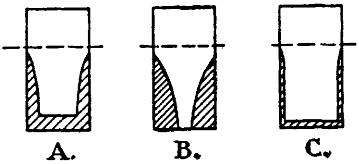
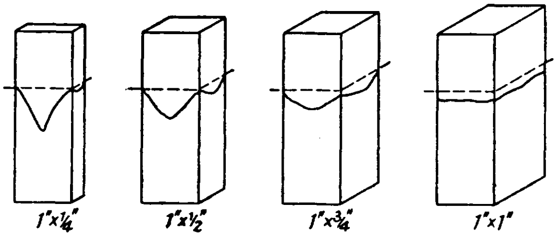


FIG. 2.



Showing the effect of thickness of specimens on distribution of corrosion in KCl *solution.*

In order to estimate the relative amounts of the corrosion on the upper and the lower face of the specimen, a compound specimen was made. This consisted of two similar steel plates, each 2″ × 1″ × 1/16″, which were prepared in the usual way; one face of each was covered with an alcoholic solution of bakelite, and when they were nearly dry, the two varnished faces were pressed together. In some experiments a piece of waxed paper was placed between the two steel plates in order that there should be no electrical contact between them, and in others the unimmersed parts of the plates were bolted together; these modifications, however, had no effect on the results.

By weighing each plate before the experiment and also after it had been electrolysed in cyanide solution in order to remove the corrosion product (as recommended by Hatfield and Shirley, " 1st Report of the Corrosion Committee of the Iron and Steel Institute," p. 207), the corrosion that had occurred on each surface was determined. After 24 hours' partial immersion in $N/10$-potassium chloride solution at 45°, the losses in weight of the upper and the lower plate were 0·0108 g. and 0·0028 g. respectively. This experiment was repeated with an $N/10$-potassium chloride solution containing a trace of phenolphthalein. It was then found that after 3 minutes' immersion the under surface of the specimen was covered evenly with alkali while the upper surface had alkali only on the central portion; this distribution persisted throughout the experiment. The experiment was repeated with a deaërated solution, with the same results.

The effect of carbon dioxide dissolved in the solution on the distribution of corrosion was also examined. It was found that when plates were immersed at 45° in an *N*/10-potassium chloride solution saturated with carbon dioxide at 25°, attack took place all over the immersed area, the region of maximum attack being at the water-line. If it is assumed that the carbon dioxide lowers the alkali concentration at the surface of the plate, this attack at the water-line is in accordance with the suggestion put forward in Part I. When the carbon dioxide had a concentration of one-tenth of the saturation value, the corrosion upon the lower surface was uniform all over the immersed area, while that on the upper was unaffected by the carbon dioxide and was as shown in Fig. 1(*B*).

DISCUSSION.

The view that the distribution of corrosion is governed by the alkali distribution was put forward by Bengough and Wormwell (*Proc. Roy. Soc.*, 1933, *A*, **140**, 407) to account for a number of their experiments, but in order to demonstrate this an experiment is described in which steel specimens are immersed in an *N*/2-sodium chloride solution saturated with boric acid as a buffer. Unfortunately, ferrous borate is insoluble, and boric acid could act as an inhibitor.

Evans and Hoar (*loc. cit.*) have investigated whether the cathodic reaction proceeds equally over the whole of the protected area or is confined to certain parts, and they have found that practically the whole of the cathodic reaction is confined to the neighbourhood of the meniscus. The question therefore arises as to how it is that the protection extends in the " ideal distribution " outside this area. Evans (private communication) has stated that it is " due to the descent of alkali from the water-line strip. In the presence of alkali very little oxygen is needed for protection, and doubtless the necessary trace of oxygen would be brought down by the descending liquid." Even if it is true that the protection is due to this trace of oxygen brought down by the descending alkali, the fact remains that it is the distribution of the alkali which governs the distribution of this oxygen and hence the corrosion.

It can be seen, therefore, that Evans, Bengough, and their co-workers are in agreement with the view that the "ideal distribution" is due to alkali distribution, and it is clear from the experiments recorded above on specimens of different thickness that if this is accepted, the explanations put forward to account for the corrosion along the vertical edges in terms of "weak points" are unnecessary. Evans's remark (above) raises the question as to the formation of anodic and cathodic areas and whether they are due to oxygen or to the alkali. Bengough and Wormwell (*loc. cit.*) maintain that the alkali gives rise to a protective film which causes the metal to become cathodic to the uncovered metal, hence the film distribution view of corrosion; but Evans, Bannister, and Britton (*Proc. Roy. Soc.*, 1931, *A*, **131**, 356) have pointed out that the electric currents involved in the corrosion process may be set up by differences in oxygen concentration which cause the aërated part of the metal to be cathodic and the unaërated part anodic, hence the theory of differential aëration.

Evans and Hoar (*loc. cit.*), after concluding that practically the whole of the cathodic reaction is confined to the neighbourhood of the meniscus, go on to state that : " The fact that the meniscus zone is the only part of the specimen which is likely to be kept replenished with oxygen makes this conclusion reasonable. Moreover, a good explanation is obtained for the curious observation that anomalous specimens which show abnormally large anodic areas owing to the development of central weak points, nevertheless show the same velocity of corrosion as other specimens which do not develop corrosion in the central area." In other words, under conditions of normal aëration, as long as the specimen passes through the meniscus the velocity of corrosion should be the same. This conclusion is not in accordance with the results of the experiment on plates inclined at 45°, since if the above were true, the amount of corrosion which has occurred should be the same on the upper and the lower face of the specimen. It has been shown that the inclination of the specimen has affected the distribution of alkali, but there seems no reason to believe that it has affected the differential aëration, especially as both surfaces of the specimen cut the meniscus.

The results recorded above do not cast doubt on Evans's experimental work, for in a large number of his experiments measurements were made when corrosion had commenced, and such experiments do not indicate the cause of the corrosion but only the way in which it proceeds. That the process is electrochemical and certain laws govern the flow of current between the anodic and cathodic areas appears to have been firmly established. But this problem must not be confused with the question as to how the anodic and cathodic areas are first formed. The theory of differential aëration is based on a number of modified "key" experiments (see Evans, "Corrosion of Metals," 1926, p. 80; *Proc. Roy. Soc.*, 1931, *A*, **131**, **358**) in which two electrodes of iron are immersed in *N*-potassium chloride solution, and one subjected to aëration. The current flowing between them is determined and shown to correspond with the weight loss. It is stated: "It is doubtful whether any metal other than iron is suitable for testing the correspondence between current and weight loss." It is suggested that the reason for this is that the following reaction takes place: $2Fe^{\cdot\cdot} + O_2 + 2H_2O \longrightarrow 2Fe^{\cdot\cdot\cdot} + 4OH'$; the resulting hydroxyl ions form a film on the metal and prevent the passage of more iron ions into solution. They therefore pass into solution at the other electrode, and naturally the weight loss corresponds to the current which has passed. It is possible therefore that differential aëration is only a particular example of film distribution.

The experiment in which a steel specimen was partly immersed at 45° in a solution of potassium chloride containing 10% of its saturation value of carbon dioxide indicates that the concentration of alkali is greater on the upper than on the lower surface. The conclusion from this is that the oxygen supply to the upper surface is greater than to the lower. If Bengough's view is accepted that the amount of corrosion is governed by the total oxygen supply, an explanation is afforded of the amount of corrosion which has occurred. It is to be noted that under these conditions the theory of differential aëration predicts the maximum corrosion on the lower or less aërated surface. Moreover, the criticisms which have been made of Bengough's experiments are not applicable to the experiments recorded above, since the conditions of aëration and the duration of the experiments are similar to those used by Evans himself.

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