87. *Some Aspects of the Modern Theories of Corrosion. Part I. Water-line Corrosion.*

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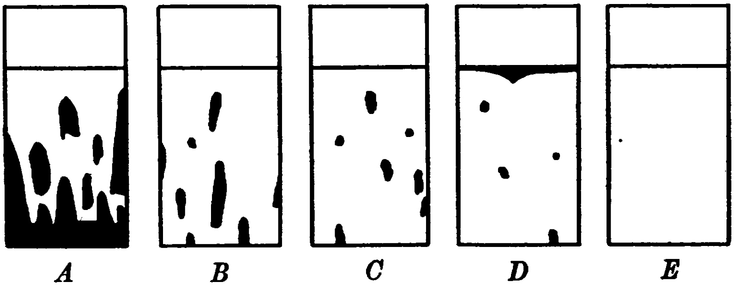
THE distribution of corrosion on steel plates partly immersed in *N*/10-potassium chloride solution was investigated by Evans and his co-workers, who attributed the corrosion to " electric currents set up by differences in the liquid, notably differences in oxygen concentration, which cause the aerated part of the metal to be cathodic and the unaerated parts to be anodic " (*Proc. Roy. Soc.*, 1931, *A*, **131**, 355). Later (*ibid.*, 1932, **137**, 345), they showed that this mechanism gives rise to a protected band along and below the water-line, which, in the centre of the specimen, extends for some distance downwards. If, however, a small quantity of sodium carbonate is added to the chloride solution, severe corrosion may take place at the water-line (see Fig. 1, taken from Evans, " Corrosion of Metals," 1926, p. 114). This local attack cannot be directly explained by the principle of differential aeration, and in order to account for it, Evans has pointed out that under certain conditions the protective films on the metal may fail, forming a " box " with a flap floating on the surface; differential aeration can be set up inside this box, giving rise to water-line attack. The reason for the failure of the film is not clearly explained, however.

FIG. 1.



Effect on the corrosion of steel produced by adding increasing quantities of sodium carbonate to a chloride solution (Evans).

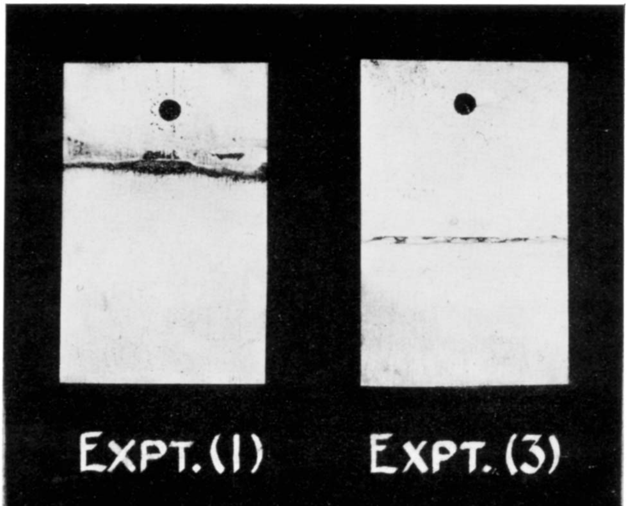
Bengough and Wormwell (*ibid.*, 1933, **140**, 408), on the other hand, attribute water-line attack to " the breakdown of the protective film by wetting and drying and by the action of carbon dioxide and other acid gases in the atmosphere." Hedges (J., 1926, 831) observed water-line attack when magnesium, zinc, and aluminium were attacked by various acids, even in an atmosphere of hydrogen. He therefore concluded that it was due, not to the action of oxygen, but to an enhanced reactivity of the solvent at the surface. This is in accordance with the conclusions of Spring (*Z. physikal. Chem.*, 1889, **4**, 658), who observed the same effect when calcite was dissolved in dilute hydrochloric acid.

In all the above examples, attack has taken place at the surface simultaneously with attack on the rest of the specimen. In order to discover if a type of attack existed which occurred only at the surface of the solution, the distribution of corrosion on steel plates partly immersed in a number of neutral solutions in a vacuum was examined.

EXPERIMENTAL.

The apparatus consisted of a vacuum desiccator, in which was placed a 400-c.c. beaker to contain the solution under examination. The steel specimens, measuring 8 × 5 × 0·04 cm. and cut from annealed mild-steel plate, were polished with No. 1 emery, degreased with carbon tetrachloride, and stored in a desiccator over calcium chloride until required; they were then suspended in the solution by means of a glass hook hanging from a glass rod. The desiccator was evacuated by means of a Hyvac pump, and it was necessary to place air-free water in the desiccator outside the beaker, in order to prevent the surface of the solution from being disturbed by bubbles rising when the pressure became low.

The solutions were rendered air-free by about 10 minutes' boiling in a flask with a narrow



EXPT. (1)   EXPT. (3)

FIG. 2.

outlet tube; this tube was then sealed, the flask allowed to cool, the seal broken, and the solution rapidly poured into the beaker. A small manometer was placed inside the desiccator to detect leaks. Each specimen was partly immersed in each solution in a vacuum for one week.

In *N*/10-potassium chloride, at the end of a week, corrosion had occurred along the water-line, and a dark green product had been formed [see Fig. 2, Expt.(1)]; the rest of the plate was only slightly tarnished, doubtless owing to a trace of oxygen in the solution. This is in accordance with the fact that the solution turned slightly brown during the first day of the experiment, but subsequently did not appear to change. At the end of the experiment, the solution contained ferric iron, and after standing in the air for some time, it became much browner. If, during the experiment, air leaked into the desiccator, a small quantity of black corrosion product was formed at the water-line, and below this the plate became evenly corroded; if more air leaked in, water-line attack disappeared altogether, and the distribution of corrosion was in accordance with the work of Evans on partly immersed plates under normal conditions. Steel partly immersed in distilled water under these conditions gave no signs of corrosion after 1 week's immersion.

The effect of a number of different solutions (*N*/10) was next examined. Potassium bromide, iodide, nitrate, or sulphate gave rise to water-line corrosion, but potassium chlorate, hydroxide, carbonate, or chromate, or disodium hydrogen phosphate did not.

In *N*/1000-solution, potassium chloride gave no perceptible corrosion at the water-line, but in *N*/100-solution it gave a fine line of corrosion product.

The effect of addition of ethyl alcohol to the solution was also examined, the following experiments being conducted simultaneously on steel plates: (1) in *N*/10-potassium chloride; (2) in aqueous alcohol of a concentration (mol.-fraction of alcohol = 0·2) at which the curve showing adsorption of alcohol at the surface of the water attains a maximum (Rideal and Schofield, *Proc. Roy. Soc.*, 1925, *A*, **109**, 61); (3) in a solution of the same aqueous alcohol which was also *N*/10 with respect to potassium chloride. In (1), considerable corrosion took place; in (2), a slight dark discoloration appeared at the water-line; and in (3), slight water-line corrosion took place, but considerably less than in (1) (see Fig. 2).

DISCUSSION.

Water-line corrosion is a chemical process, and for this reason only examples in which chemical attack has taken place have been quoted in the introduction. Results obtained by Klobukow (*Z. physikal. Chem.*, 1890, 5, 180), Beckhold (*ibid.*, 1890, 5, 68), and Gurwitsch (*ibid.*, 1924, **109**, 375) have been neglected, as they refer to physical solution, and this phenomenon has not been investigated in this paper.

It has been shown that iron immersed in *N*/10-potassium chloride in a vacuum is converted at the water-line into ferrous hydroxide, a reaction which does not take place if the iron is completely immersed under the same conditions. In order to explain this reaction it is necessary to postulate the existence of an electric current. Now, Frumkin (*ibid.*, 1924, **109**, 34) has shown that a potential exists at the surface of a number of electrolytes in water, and this affords a feasible explanation of the above examples of water-line attack. In the cases of chemical surface attack recorded by Spring and by Hedges (*locc. cit.*), the surface of the solution was disturbed by bubbles, and it is suggested that it was the potential which existed in the surface of these bubbles, together with that at the free surface of the solution, which gave rise to the observed phenomenon. This will also account for Spring's observation that when carbon dioxide, air, or hydrogen is allowed to impinge on a calcite crystal immersed in dilute hydrochloric acid, perforation of the crystal takes place at the point of impingement.

The effect of the potential when imposed upon the steel specimen in presence of potassium chloride, bromide, iodide, or sulphate solution would be the production of a soluble ferrous salt, together with potassium hydroxide. The latter would react with the ferrous salt, yielding the green corrosion product observed. It is unfortunate that a trace of air was always present in the solution during these experiments, as this prevented any accurate measurements of the amount of corrosion which had taken place. It cannot be argued, however, that the corrosion observed at the water-line was due to this trace of oxygen, for no corrosion was observed when distilled water was used. Also, since it is easier to pump air out of a desiccator than to remove it from a solution, this trace of oxygen would be in the solution, and the depolarising action of the oxygen would be uniform all over the plate. Further evidence is to be found in the results of Evans and Borgmann (*Z. physikal. Chem.*, 1932, **160**, 197), who obtained a green corrosion product at the water-line on steel plates partly immersed for 2 days in oxygen-free potassium chloride solution in atmospheres of hydrogen and nitrogen. Now, if a solution of potassium chlorate, hydroxide, carbonate, chromate, or disodium hydrogen phosphate is added to one of a ferrous salt, an insoluble precipitate is formed. The action of the potential at the surface, therefore, would result in the production of an invisible film on the metal as a primary product which would prevent visible corrosion. Experiments were performed with a mixed solution $N/10$ with respect to both potassium chloride and potassium hydroxide, but the results were erratic : sometimes very slight corrosion took place at the water-line, and at other times it was completely inhibited.

The question now arises as to why water-line corrosion does not take place on partly immersed steel plates under normal conditions. Evans (*ibid.*, 1932) has shown that one of the first results of corrosion of steel so immersed in potassium chloride solution under normal conditions is the production of potassium hydroxide just below the surface of the solution. This alkali would prevent attack at the water-line. Water-line corrosion in a chloride solution in the presence of sodium carbonate (as in Fig. 1) can, however, be accounted for similarly. In these experiments we have two sources of alkali which are capable of inhibiting corrosion at the water-line : (1) the added sodium carbonate, which increases from A to E ; (2) the alkali formed during the corrosion process, which is proportional to the amount of corrosion which has taken place and clearly decreases from A to E. The specimen D, then, is the one in which the sodium carbonate added to the solution is insufficient to prevent water-line attack, but sufficient to inhibit corrosion of the normal type.

The experiment showing the prevention of water-line attack by the addition of alcohol to the solution is in accordance with the work of Ganguly and Banerji (*Z. anorg. Chem.*, 1922, **124**, 140), who considered that the enhanced reactivity of the solvent at the surface was related to the surface tension of the liquid. This indicates that the attack is related to adsorption of the solute at the surface of the solvent, which takes place in accordance with the Gibbs equation.

SUMMARY.

When a specimen of steel is partly immersed in a de-aerated $N/10$-solution of potassium chloride in a vacuum, attack takes place at the water-line. This is not explained by the present theories of water-line corrosion. It is suggested that it is due to the potential existing at the surface of the solution. Since this water-line attack is depressed by the presence of ethyl alcohol in the solution, it is suggested that it is connected with the negative adsorption of the solute at the surface of the solvent.

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