

the attack being enormously enhanced by oxygen. When iron rods (not provided with rubber bands) were immersed in the acid in the presence of oxygen, corrosion penetrated longitudinally from the two ends along the center of the rods, producing an effect like a hollow tree; if pressed between the fingers after this treatment, the sides of the rod could be caused to collapse, so that the whole crumbled.⁵ This penetration of corrosion along internal paths, causing rottenness of the material even when the outer parts are apparently little changed, is of course a special feature of differential aeration attack. It would seem that in McCulloch's experiment the intense attack in the capillary channel below the rubber band is also due mainly to differential aeration, the attack being localized at the anodic points relatively inaccessible to oxygen, while the aerated surface outside the band forms the cathode. The present writer would be the last to deny the importance of capillary forces in some types of corrosion, having indeed attributed to such causes the localized corrosion of iron in chloride-chromate and chloride-carbonate mixtures,⁶ which cause attack to be concentrated mainly at the water line or at the margins of drops. However, capillary action appears to play but little part in the case described by McCulloch.

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The Rapid Corrosion of Metals by Acids within Capillaries. Reply to Ulick R. Evans.—In the note on "Corrosion of Metals by Acids within Capillaries"¹ it should have been made clear that the effect described was believed not to be due at all to differential aeration, but to differ from the well-known cases of pitting from the latter cause.

The writer has repeated the procedure described by Evans in the preceding note, using the same test-pieces (rivets), wrapped with rubber bands, as shown in the first note.¹ (These were first cleaned from scale by a short dip into concd. hydrochloric acid.) Three 1-liter bottles were used, each containing about 250 cc. of 1.4 *N* hydrochloric acid, which had been previously boiled and cooled in a vacuum. One bottle was left exposed to the air, one had the air replaced by hydrogen, and the third by carbon dioxide. The latter two were sealed with rubber stoppers, through which glass tubes permitted the escape of gas beneath the surface of mercury. The test was continued for four days.

In a later experiment, the conditions were made more completely air-free by letting boiled acid flow from an evacuated flask into another evacu-

⁵ The "hollow-tree phenomenon" was not caused by the protective action of scale, since the rods were abraded with emery just before immersion.

⁶ Evans, *J. Soc. Chem. Ind.*, **43**, 315T (1924); **44**, 163T (1925).

¹ McCulloch, *THIS JOURNAL*, **47**, 1940 (1925).

ated flask (300 cc.) containing four of the rivets. When the latter flask was completely filled, a rubber tube dipping beneath mercury was cut to make a way for hydrogen to escape. A parallel test was made with some of the same acid to which air was admitted.

The writer agrees with Evans that the grooving about the rubber bands is less distinct in the air-free acid than it is when air is present, but he does not find that the effect ceases to exist at all. The fact that the grooves are less distinct is attributed to a more rapid attack of the surface as a whole, rendering the action within the capillary spaces less only by comparison.

It is admitted that differences in oxygen concentration, where such exist, may be a contributing cause, but not the principal cause of the capillary corrosion. There may be electrolytic action due to the lowering of hydrogen concentration in the neighborhood of bubbles resting upon an oxygen-free surface. Further work should be done to find out how important this effect may be.

There is a marked difference in the manner in which the air-free acid acts upon the iron surfaces. The air-free acid attacks the surface smoothly and uniformly, while the aerated acid acts more strongly within the pores of the metal. Measurement was made of the decrease in thickness of the exposed portions of the rivets under the two conditions. The average decrease in the aerated acid was in the two experiments 0.025 mm. and 0.05 mm. In the air-free acid the losses were 0.25 mm. with carbon dioxide, 0.175 mm. and 0.10 mm. with hydrogen. The losses in weight were not concordant, however, for in the first experiment, five rivets in aerated acid lost 1.68 g., and five under hydrogen, 2.59 g., while in the second experiment, four in aerated acid lost 4.14 g., and four in air-free acid 4.03 g. These erratic weights may be explained by variations in structure of the iron, rendering it easier for the acid to attack between the fibers in some pieces than in others. It is plain that there is much room for further work upon these problems.

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An Improvement of the Cobalt Aluminate Test for Aluminum.—When a supposed precipitate of aluminum hydroxide is dissolved in nitric acid, treated with a few drops of cobalt nitrate and then reprecipitated and ignited on a platinum wire according to the method given by Noyes¹ great dexterity is required to prevent the precipitate, which shrinks on ignition, from falling off the wire. The foregoing procedure is a modi-

¹ Noyes, "Qualitative Chemical Analysis," MacMillan, 1922, 9th ed., p. 99.