on the steel exposed at the scratch line; this film afforded protection even when the cathodic treatment had ceased. The value of galvanized coatings in protection against cold water may be partly due to the films thrown down by cathodic action (2) by operation of the cell zinc | iron. The polarity of this cell reverses after several days in water at ordinary temperature (9) and much more rapidly at 70° C. (10). The reversal does not necessarily interfere with protection at discontinuities in the coat, at least against cold water, since the film formed during the period before reversal may continue to give protection.

SAFE AND DANGEROUS INHIBITION SYSTEMS

From the foregoing it appears that, in general, anodic inhibitors are efficient but dangerous, while cathodic inhibitors are inefficient but safe. Attempts made to obtain a system which would be both safe and efficient, by using cathodic and anodic inhibitors concurrently, have been only partially successful (11). Later attempts have been made to obtain the desired result by using anodic and cathodic inhibitors alternately; the results are more encouraging, but a pronouncement on the matter would be premature.

Circumstances are, however, known where even a cathodic inhibitor may intensify attack. One such case is discussed in this symposium by Thornhill (page 706), who shows that certain salts bring the attack to the water line—i.e., near the source of oxygen, where otherwise it would be well below the water line; this shift in the site of attack is accompanied by greater local intensity. But there are situations where any inhibitor—cathodic, anodic, or general—which covers the greater part of the surface with a protective layer may, in time, lead to intensified attack.

Consider two closed iron boxes completely filled with water, which remains until all the oxygen, carbonic acid, and other corrosive substances present have become exhausted; in the first box the whole of the metallic surface is exposed to the water, but in the second, 90% is covered with a protective layer. The final corrosion produced will be the same in both boxes, although in the second box it may require a longer time for completion; but since the corrosion in the second box is confined to one tenth of the original area, it will in the end be more intense than that in the first box, whatever the mechanism of attack or the nature of the protective film may be.

Localization of attack possesses considerable importance in connection with the corrosion of boilers. Turner (12) reports that the presence of mill scale on the surface of boiler tubes tends to produce pitting at breaks in the scale. The reason is clear. The scale will constitute a large cathode, and the steel exposed at the discontinuities in the scale will be a small anode. Any oxygen reaching the large scale-covered surface will act as cathodic stimulator, and the current flowing will produce anodic attack at the breaks in the scale. Since this attack is concentrated on a small area, it is liable to be intense and lead to pitting.

Vernon and Wormwell (13) point out that the presence of magnesium and calcium salts in the water (particularly sulfates) can lead to pitting, apparently by producing an oxide scale not unlike mill scale and capable of acting in the same way. The fact that such salts lead to the production of a compact oxide scale may perhaps be explained as follows: In the author's research (4) on the corrosion of steel specimens partly immersed in magnesium sulfate solution at ordinary temperatures, it was noticed that a bright green clinging deposit was formed at places which apparently had been cathodic but were becoming anodic. This was probably a hydrated magnetite (with some ferrous ions replaced by magnesium ions, which explains the unusually bright green color) formed in the presence of a restricted quantity of oxygen by the action of ferrous sulfate, the anodic product, upon the layer of magnesium hydroxide which had previously been deposited by cathodic action. Under the conditions of the author's experiments, the green substance was subsequently oxidized to

pale brown rust still containing magnesia (hence the unusual paleness); but under boiler conditions it would probably suffer dehydration and give a conducting layer of anhydrous magnetite, which would act in the same way as mill scale in producing pitting.

This seems to afford a satisfactory explanation of the fact that magnesium salts, which undoubtedly diminish corrosion at ordinary temperatures under half-immersed conditions where the adherent product is unsuited to act as a cathode, may, under boiler conditions where the product is compact and probably conducting, give rise to dangerous pitting.

LITERATURE CITED

(1) Bauer, O., and Wetzel, E., *Mitt. deut. Materialprüfungsanstalt.*, 34, 347 (1916); Bauer, O., and Schikorr, G., *Ibid.*, **Sonderhefte 28**, 69 (1936); Schikorr, G., *Korrosion u. Metallschutz*, **16**, 181 (1940).
(2) Britton, S. C., *J. Soc. Chem. Ind.*, 55, 19T (1936).
(3) Evans, U. R., *Ibid.*, 43, 315 (1924).
(4) *Ibid.*, 47, 57T (1928).
(5) Evans, U. R., *Trans. Electrochem. Soc.*, 69, 213 (1936); Chyzewski, E., and Evans, U. R., *Ibid.*, 76, 215 (1939).
(6) Hoar, T. P., and Evans, U. R., *J. Chem. Soc.*, 1932, 2476.
(7) Mayne, J. E. O., and Evans, U. R., *Chemistry & Industry*, 1944, 109.
(8) Mears, R. B., and Evans, U. R., *Trans. Faraday Soc.*, 31, 527 (1935).
(9) Roters, H., and Eisenstecken, F., *Arch. Eisenhüttenw.*, 15, 59 (1941).
(10) Schikorr, G., *Trans. Electrochem. Soc.*, 76, 247 (1939).
(11) Thornhill, R. S., and Evans, U. R., *J. Iron Steel Inst.* (London), 146, 73 (1939).
(12) Turner, T. H., *Proc. Inst. Mech. Eng.* (London), 149, 77 (1943).
(13) Vernon, W. H J., and Wormwell, F., *Ibid.*, 150, 111 (1943).

Discussion of Paper
by U. R. Evans

D. S. McKINNEY AND J. C. WARNER
Carnegie Institute of Technology, Pittsburgh, Pa.

SEVERAL questions will be raised to make clearer the interpretation of Dr. Evans' paper. In the first place, the interpretation of corrosion phenomena would be improved by treating all anodic and cathodic reactions, as well as the so-called secondary reactions, from the ionic standpoint. For example, the author states: "Iron suffering electrochemical corrosion in sodium chloride solution will yield ferrous chloride and sodium hydroxide as anodic and cathodic products, respectively, and these will interact a short distance from the site of attack." We prefer to say: "Iron suffering electrochemical corrosion will yield ferrous ion and hydroxyl ion as anodic and cathodic products, respectively, and these will interact at a short distance from the actual site of attack."

The author defines anodic inhibitors and cathodic inhibitors as substances which will yield either a sparingly soluble anodic body or a sparingly soluble cathodic body, respectively. He does admit that inhibition may be caused by adsorbed substances such as those which are effective in the pickling of iron and steel. We would prefer a broader definition—namely, that any substance be considered an inhibitor which serves to increase anodic or cathodic polarization.

Further amplification of the author's explanation of the action of chromates as anodic inhibitors seems desirable. When one considers the fact that chromic salts are relatively poor inhibitors, his explanation of the action of chromates through the formation of a hydrated ferric-chromic oxide film appears to be inadequate.

We would also like to call attention to the fact that the alkaline

character of many anodic inhibitors is more or less incidental. The important point seems to be that the pH must be sufficiently high to give a reasonable concentration of the inhibiting anion.

In the author's example to show that corrosion would be more intense in the one of two iron boxes which had 90% of its surface covered with protective coating, other conditions being equal, it is implied that corrosion will cease when all oxygen and carbonic

acid have become exhausted. It seems important to emphasize that the corrosion of iron in contact with pure water to form either ferrous hydroxide or magnetite is spontaneous, the formation of the latter corrosion product corresponding to the more spontaneous reaction[1].

[1] Corey, R. C., and Finnegan, T. J., *Proc. Am. Soc. Testing Materials*, **39**; 1257 (1939); Thompson, M. deK., *Trans. Electrochem. Soc.*, **78**, 251 (1940), Warner, J. C., *Trans. Electrochem. Soc.*, **83**, 319 (1943).

Reply to Discussion

U. R. EVANS

IT IS equally correct to regard the corrosion products as either (a) ferrous chloride and sodium hydroxide or (b) ferrous ions and hydroxyl ions; it is well known that sodium hydroxide dissociates in solution into sodium and hydroxyl ions, and one sort of ion cannot exist without the other. Which form of expression is most helpful depends on the nature of the argument and, perhaps, the temperament of the audience being addressed. In the present case it is more informative to call the anodic product ferrous chloride than ferrous ions. The course of attack may sometimes be affected by the nature of the anion with which the metallic cation is paired; for instance, ferrous sulfate is more likely to become supersaturated and separate out than is ferrous chloride, and, as shown by W. J. Müller, such separation may be the first stage of passivity.

The fact that chromic salts are relatively poor inhibitors is not inconsistent with the view that the good inhibition by chromates is due to the precipitation of hydrated ferric-chromic oxide over anodic points. The obstructive action of a precipitate depends, not so much on what is precipitated, as on where it is precipitated. In the case of chromic salts, chromic hydroxide is thrown down on the cathodic zone and fails seriously to hinder attack; in the

case of the chromate, the mixed hydroxide is precipitated locally at places where anodic attack would otherwise set in and prevents it from developing. The barrier needed to prevent anodic action is essentially a type impervious to ions, whereas that needed to prevent cathodic action must be impervious to electrons. Cases are known where films of considerable thickness have formed over the cathodic zone, which, although possessing electronic conductivities, provide no hindrance to the electrochemical action.

That corrosion of iron by water may continue even when oxygen and carbonic acid are absent is generally admitted, and credit is due J. C. Warner for pointing out that this is thermodynamically possible, as well as to the other authors quoted for showing that it actually does occur. However, the hydrogen-evolution type of attack produced by neutral water is frequently slow compared to the corrosion produced in the presence of oxygen or acid, and the hypothetical example used in showing that intensification is sometimes possible with any film-forming inhibitor, whatever its mechanism, appears to be legitimate even if it represents an oversimplification of the state of affairs commonly encountered in practice.

Zinc, Manganese, and Chromic Salts as Corrosion Inhibitors

R. S. THORNHILL[1]

Cambridge University, England

DATA are presented showing that the rate of corrosion of steel in tap water is reduced by adding small quantities of zinc and manganese salts; chromic salts bring about a certain measure of inhibition at low, but not high concentrations. At relatively high concentrations of zinc and chromium, marked intensification occurs in the water-line zone; manganese salts are free from this defect, since the water-line zone is not attacked. Zinc and chromic salts must, under some circumstances, be regarded as "dangerous" inhibitors.

THE addition to corrosive waters of small quantities of certain chemicals to minimize corrosion has been common industrial practice for many years. Probably the first reference to the beneficial effect of certain metals in solution was that of Parker (7) in 1881 who, in the course of experiments on the prevention of corrosion in boilers by zinc protectors, came to the

[1] Present address, Imperial Chemical Industries, Ltd., Winnington, Northwich, Cheshire, England.

conclusion that much of the success must be ascribed to zinc salts. The beneficial effect of zinc salts was later recorded by Evans (2) in experiments on drop corrosion; protective treatments for magnesium and steel depending on the precipitation of a film of zinc hydroxide have also been developed (5, 9). In some of these cases the deposition of zinc hydroxide arises through the formation of alkali at the corrosion cathodes; presumably the hydroxides of other metals should behave in a similar manner.

A further important class of inhibitor relies upon the formation of insoluble bodies with the anodic products of corrosion. In this class are the chromates, phosphates, and silicates.

In choosing an inhibitor from one of these groups, it is important to remember that inhibition may result in (a) diminution in the corroded area and (b) reduction in the corrosion rate; if effect a exceeds b, there will be an intensification of attack; thus certain inhibitors may be "dangerous". Evans (3) concludes that inhibitors which function by the deposition of material on the cathode are likely to be "safe", in that no intensification should