# **840.** *The Effect of Inhibitors of the Corrosion of Iron on the Air-formed Film.*

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The effect of 0·1N-sodium benzoate, acetate, borate, carbonate, and hydroxide on the air-formed film on pickled mild steel, pickled iron, or iron reduced in hydrogen, was determined electrometrically.

The air-formed film was reinforced and thickened by material of similar composition to the extent of 20—120%, depending upon the inhibitor and the surface condition of the metal.

Iron or mild steel exposed to air becomes covered with an oxide film 26—40 Å thick[1] which is always permeable to iron ions, since however long iron may have been in contact with the air, it always corrodes when immersed in water. But when iron, carrying its air-formed film, is immersed in 0·1N-sodium hydroxide, carbonate, borate, acetate, or benzoate it does not corrode, indicating a change in the permeability of the oxide film.

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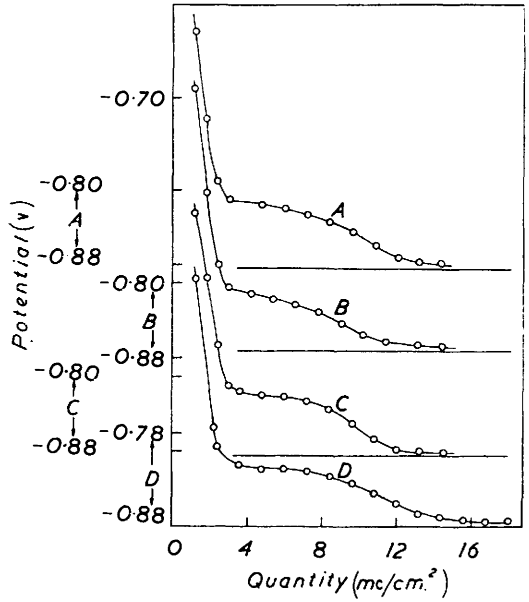
[1] Hancock and Mayne, preceding paper.

The composition of the film formed by these inhibiting solutions has been established. The air-formed film was first removed from iron specimens with dilute acid, the acid was then displaced by a large volume of the inhibiting solution,[2] which was saturated with air, and the iron was left in contact with the solution for 1—2 days. The film was then removed and shown by electron diffraction to be an anhydrous cubic oxide of similar composition to that of the air-formed film. It was concluded that the anhydrous cubic oxide was derived from the inhibitive ions in solution, but later it was thought that the air-formed film might have been rapidly re-formed by the air dissolved in the solution; inhibition might then have occurred owing to repair of weak spots in the air-formed film by oxidation of insoluble compounds derived from the inhibitive anions.[3] If the final film contained less than 10% of these compounds they might not have been detected by electron diffraction and the oxide film would not have been appreciably thickened by the inhibiting solutions.



Potentials are on the hydrogen scale.
*A*. Sodium benzoate.
*B*, Sodium borate.
*C*, Sodium carbonate.
*D*. Sodium hydroxide.

The thickness of the films on iron and mild steel before and after treatment with inhibiting solutions has now been measured electrometrically.[1]

## Experimental

Compositions of iron and mild steel and methods of pickling or reduction in hydrogen were as before.[1]

The specimens were pickled or reduced simultaneously, then stored in a desiccator ($CaCl_2$) for 24 hr., then totally immersed in the inhibiting solutions. At intervals during 1—18 days, specimens were withdrawn, washed six times with absolute alcohol, dried on filter paper, and cathodically reduced. Experiments with sodium acetate and iron were done later, but as nearly as possible under the same conditions.

Cathodic reductions were carried out in 0·2N-potassium chloride, deaerated by six cycles of flushing and boiling under vacuum. The constant current density was 40 μA/cm.² and potentials were measured every 15 sec.

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[2] Mayne, Menter, and Pryor, *J.*, 1950, 3229; Mayne and Menter, *J.*, 1954, 99 (NaOH), 103 ($Na_2CO_3$, $Na_2B_4O_7$); Menter, unpublished work (NaOAc); Chemistry Research, 1950, H.M.S.O., London, 1951, p. 19 (NaOBz).

[3] Mayne, *Chem. and Ind.*, 1953, 538.

Results for pickled iron are given in Table 1 and a typical set of potential–time curves for four inhibiting solutions is shown in the Figure. Tables 2 and 3 give the results obtained with pickled mild steel and hydrogen-reduced iron.

TABLE 1. *Pickled iron.*

| $t$[a] (days) | $A$[b] (mv) | $H_2$[c] (mv) | $Q$[d] (mc/cm.$^2$) | $F$[e] (Å/appar. cm.$^2$) | $t$[a] (days) | $A$[b] (mv) | $H_2$[c] (mv) | $Q$[d] (mc/cm.$^2$) | $F$[e] (Å/appar. cm.$^2$) |
|---|---|---|---|---|---|---|---|---|---|
| 0·1N-Sodium benzoate, pH 7·1; thickening[f] 40% | | | | | | | | | |
| 1 | −818 | −888 | 8·5 | 47 | 9 | −828 | −874 | 9·6 | 53 |
| 1 | −820 | −866 | 9·0 | 50 | 16 * | −832 | −886 | 10·9 | 61 |
| 1 | −820 | −880 | 9·5 | 53 | 16 * | −838 | −888 | 12·3 | 68 |
| 2 | −825 | −872 | 9·6 | 53 | 18 * | −830 | −892 | 11·4 | 63 |
| 3 | −812 | −868 | 9·6 | 53 | Average | −824 | −880 | 10·05 | 56 |
| 5 | −820 | −882 | 10·2 | 57 | | | | | |
| 0·1N-Sodium acetate, pH 8·42; thickening 40% | | | | | | | | | |
| 1 | −825 | −890 | 10·0 | 56 | 4 | −827 | −872 | 10·0 | 56 |
| 1 | −804 | −860 | 10·8 | 60 | Average | −819 | −874 | 10·1 | 56 |
| 1 | −820 | −874 | 9·6 | 53 | | | | | |
| 0·1N-Sodium borate, pH 9·2; thickening 35% | | | | | | | | | |
| 1 | −812 | −876 | 10·8 | 60 | 5 | −810 | −880 | 8·8 | 49 |
| 1 | −814 | −868 | 9·0 | 50 | 15 | −818 | −870 | 10·0 | 56 |
| 1 | −810 | −890 | 8·5 | 47 | 15 | −818 | −874 | 11·3 | 63 |
| 2 | −812 | −870 | 9·8 | 55 | 18 | −818 | −872 | 11·0 | 61 |
| 2 | −818 | −886 | 8·7 | 48 | Average | −814 | −877 | 9·7 | 54 |
| 3 | −810 | −880 | 8·9 | 50 | | | | | |
| 0·1N-Sodium carbonate pH 11·0; thickening 37% | | | | | | | | | |
| 1 | −826 | −893 | 8·8 | 49 | 9 | −825 | −863 | 10·2 | 57 |
| 1 | −822 | −882 | 9·5 | 53 | 11 | −828 | −903 | 10·8 | 60 |
| 2 | −829 | −890 | 9·6 | 53 | Average | −828 | −886 | 9·9 | 55 |
| 9 | −835 | −886 | 10·3 | 57 | | | | | |
| 0·1N-Sodium hydroxide, pH 12·5; thickening 59% | | | | | | | | | |
| 1 | −818 | −874 | 12·2 | 68 | 2 | −816 | −870 | 11·4 | 53 |
| 1 | −820 | −876 | 11·0 | 61 | 3 | −825 | −885 | 11·4 | 63 |
| 1 | −826 | −878 | 11·2 | 62 | 8 | −816 | −850 | 11·8 | 66 |
| 1 | −818 | −864 | 10·8 | 60 | 9 | −820 | −868 | 13·0 | 72 |
| 1 | −816 | −860 | 10·8 | 60 | Average | −820 | −870 | 11·4 | 63·5 |
| 2 | −827 | −876 | 11·0 | 61 | | | | | |

[a] Time in inhibitor (days). [b] Arrest potential. [c] Potential of evolution of hydrogen. [d] Quantity of electricity required to reduce the film. [e] Thickness of film to nearest Å. [f] Increase in film thickness due to action of inhibitor. All potentials are on the hydrogen scale.

* Mould in solution.

TABLE 2. *Pickled mild steel.*

| $t$ (days) | $A$ (mv) | $H_2$ (mv) | $Q$ (mc/cm.$^2$) | $F$ (Å/appar. cm.$^2$) | $t$ (days) | $A$ (mv) | $H_2$ (mv) | $Q$ (mc/cm.$^2$) | $F$ (Å/appar. cm.$^2$) |
|---|---|---|---|---|---|---|---|---|---|
| 0·1N-Sodium benzoate, pH 7·1; thickening 40% | | | | | | | | | |
| 2 | −784 | −890 | 9·0 | 50 | 3 | −808 | −904 | 9·5 | 53 |
| 2 | −784 | −910 | 9·5 | 53 | Average | −800 | −903 | 9·2 | 51 |
| 3 | −815 | −908 | 8·7 | 48 | | | | | |
| 0·1N-Sodium borate, pH 9·2; thickening 18% | | | | | | | | | |
| 2 | — | −922 | 7·8 | 43 | 5 | −800 | −932 | 7·6 | 42 |
| 3 | −760 | −895 | 7·5 | 42 | Average | −783 | −912 | 7·8 | 43 |
| 3 | −790 | −900 | 8·2 | 46 | | | | | |
| 0·1N-Sodium carbonate, pH 11·0; thickening 23% | | | | | | | | | |
| 1 | −784 | −916 | 7·2 | 40 | 3 | −805 | −925 | 8·5 | 47 |
| 2 | −800 | −926 | 7·5 | 42 | 5 | −830 | −932 | 9·2 | 51 |
| 3 | −783 | −910 | 8·4 | 47 | Average | −800 | −922 | 8·1 | 45 |
| 0·1N-Sodium hydroxide, pH 12·5; thickening 56% | | | | | | | | | |
| 1 | −802 | −914 | 9·1 | 51 | 3 | −807 | −921 | 9·4 | 52 |
| 2 | −814 | −908 | 11·4 | 63 | 3 | −820 | −913 | 11·4 | 63 |
| 3 | −803 | −905 | 10·0 | 56 | Average | −809 | −912 | 10·3 | 57 |

TABLE 3. *Hydrogen-reduced iron.*

| *t* (days) | *A* (mv) | $H_2$ (mv) | *Q* (mc/cm.$^2$) | *F* (Å/appar. cm.$^2$) | *t* (days) | *A* (mv) | $H_2$ (mv) | *Q* (mc/cm.$^2$) | *F* (Å/appar. cm.$^2$) |
|---|---|---|---|---|---|---|---|---|---|
| 0·1N-Sodium benzoate, pH 7·1; thickening 45% | | | | | | | | | |
| 2 | −802 | −910 | 6·5 | 36 | 3 | −808 | −920 | 6·8 | 38 |
| 2 | −798 | −892 | 7·0 | 39 | Average | −800 | −910 | 6·8 | 38 |
| 0·1N-Sodium borate, pH 9·2; thickening 51% | | | | | | | | | |
| 2 | −788 | −900 | 7·2 | 40 | Average | −790 | −905 | 7·1 | 39·5 |
| 3 | −796 | −910 | 7·0 | 39 | | | | | |
| 0·1N-Sodium carbonate, pH 11·5; thickening 95% | | | | | | | | | |
| 2 | −775 | −860 | 9·0 | 50 | Average | −790 | −880 | 9·15 | 51 |
| 3 | −803 | −904 | 9·3 | 52 | | | | | |
| 0·1N-Sodium hydroxide, pH 12·5; thickening 120% | | | | | | | | | |
| 1 | −805 | −870 | 11·0 | 61 | 3 | −820 | −920 | 10·2 | 57 |
| 1 | −795 | −900 | 10·2 | 57 | Average | −810 | −900 | 10·5 | 58 |

## DISCUSSION

Table 1, col. 2, shows that the oxide films on pickled iron were all reduced at about −0·82 v irrespective of the solution in which the specimens were inhibited; furthermore, this potential was similar to that at which the air-formed oxide film was reduced, −0·80 v, at 40 μA/cm.$^2$ (Table 1 of preceding paper); the potentials of hydrogen evolution were also the same, whether the specimens had been inhibited or not. Mild steel and reduced iron behave similarly, although sometimes the potentials of hydrogen evolution differ slightly more.

The fact that both the air-formed films and those produced by the inhibitors were reduced at the same potentials confirmed that the same material was being reduced. Further evidence that only one phase is produced during inhibition was provided by Brasher and Stove [4] who found that the benzoate content of the films produced on mild steel by sodium benzoate containing radioactive carbon was only 0·01 μg./cm.$^2$ (calc. as sodium benzoate); this value was independent of the concentration of sodium benzoate and the time of immersion. As the air-formed film on mild steel is about 37 Å thick (1·9 μg. of $\gamma$-$Fe_2O_3$/cm.$^2$) and thickens by 40% (Table 2) when immersed in sodium benzoate (equivalent to an increase of 0·8 μg. of $\gamma$-$Fe_2O_3$/cm.$^2$), the material formed by the inhibitor contains only about 1·0% of benzoate ions.

The results (Tables 1—3) indicate that the air-formed film on pickled iron thickened by 35—59% when immersed in the inhibiting solutions, on pickled mild steel by 18—56% and on iron reduced in hydrogen by 45—120%. The thickening increased with pH (clearly shown by the reduced specimens, but less definitely by pickled ones) and occurred almost entirely within the first 24 hr. of immersion, but there was slight indication that it continued slowly thereafter.

It was concluded that when pickled mild steel or iron or iron reduced in hydrogen was immersed in these solutions the air-formed film was rapidly thickened by 20—120% by formation of anhydrous cubic oxide of similar composition. Consequently inhibition cannot be attributed solely to adsorption, or to the repair of weak spots in the air-formed film; the question of how inhibitive solutions produce such quantities of anhydrous cubic oxide irrespective of their anions will be discussed elsewhere.

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[4] Brasher and Stove, *Chem. and Ind.*, 1953, 558.