

### 366. *The Passivity of Metals. Part VII. The Specific Function of Chromates.*

By T. P. HOAR and U. R. EVANS.

THE known methods of preventing corrosion of iron include the employment of (1) *chromium* in the metal, (2) *soluble chromates* in the liquid, (3) *sparingly soluble chromates* (pigments) at the interface. This recurrent use of chromium can hardly be accidental; the present paper is concerned with the specific function of the element.

Oxidising agents frequently stimulate corrosion through depolarisation at the cathodic areas, but sometimes retard corrosion by causing the secondary corrosion product to be precipitated so close to the surface as to stifle further attack. Thus, iron placed in distilled water yields at certain points ferrous hydroxide, which at a distance is converted by dissolved oxygen into the less soluble hydrated ferric oxide (rust); if through the addition of potassium chromate, or even through whirling in water saturated with oxygen, the second change is made to take place very close to the metal, attack is arrested (Evans, "Corrosion of Metals," 1926, p. 108; Evans, Bannister, and Britton, *Proc. Roy. Soc., A*, 1931, **131**, 372; compare Forrest, Roetheli, Brown, and Cox, *Ind. Eng. Chem.*, 1931, **23**, 650, 1010, 1012, 1084).

The addition of potassium chromate to potassium chloride solutions brings the site of the conversion of the primary anodic product (ferrous chloride) into rust closer to the original point of attack (1) because the precipitant (sodium hydroxide) results from a cathodic reaction which requires an oxidising depolariser, (2) because the conversion of ferrous hydroxide into rust also requires an oxidising agent. Thus increasing additions of chromate give the following stages :

(a) With little or no chromate, large mildly attacked areas appear, with flocculent rust.

(b) More chromate confines corrosion to small areas, covered by rust blisters below which the attack is intense.

(c) Further chromate brings the rust into optical contact with the metal, yielding patches of interference tints, with little or no corrosion, since the film is now protective; the tints indicate that the film produced becomes thinner as the chromate content is increased, until finally,

(d) At high chromate contents, the film is so thin as to be invisible, the metal remaining unchanged to the eye.

But if this represents the complete explanation, other oxidising

agents should produce the same effect. The experiments described below indicate that other oxidising agents have far less inhibitive power than chromates, and that the addition of sodium hydroxide and potassium chromate to ferrous sulphate (whichever is added first) yields a mixture of ferric and chromic oxides; the spinel  $\text{FeO}, \text{Cr}_2\text{O}_3$ , sometimes suggested as the cause of protection, is not produced. Furthermore, the rust obtained during partial inhibition with chromate, and the invisible film produced during complete inhibition, both contain trivalent chromium, thus suggesting that inhibition by chromates, like the immunity of chromium steels, is attributable to a mixture of chromic and ferric oxides.

## EXPERIMENTAL.

*Materials.*—The dead-mild steel used (MS 1), kindly supplied by Dr. W. H. Hatfield, contained C, 0.03; Mn, 0.38; Si, 0.01; S, 0.038; P, 0.037; Ni, 0.16; Cu, 0.05; Al, 0.01; As, 0.026%, and no chromium. It was ground with Hubert No. 1 F emery and degreased with  $\text{CCl}_4$ .

*Comparison of Oxidising Agents.*—Steel specimens measuring  $6.5 \times 2.5$  cm., abraded 24 hrs. previously, were fixed vertically in beakers 8 cm. high  $\times$  4 cm. diameter. They were immersed to a depth of 3.5 cm. for 24 hrs. at  $20^\circ$  in solutions containing KCl and either (a)  $\text{K}_2\text{CrO}_4$ , (b)  $\text{KMnO}_4$ , (c)  $\text{NaVO}_3$ , or (d)  $\text{H}_2\text{O}_2$ . The results are in Table I.

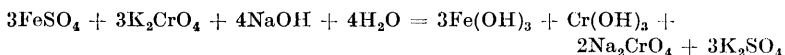
TABLE I.

Corroding medium.		
KCl, M.	$\text{K}_2\text{CrO}_4$ , M.	Type of attack.
0.1	0.001	Edge attack only: adherent brown rust.
0.1	0.01	Attack at few points on edges: rust blisters.
0.1	0.1	Slight attack at few points on edges: rust blisters.
0.1	1.0	No attack.
KCl, M.	$\text{KMnO}_4$ , M.	
0.1	0.001	General attack, except water-line.
0.1	0.01	Heavy pitting, adherent brownish-black coating.
0.1	0.1	Very heavy pitting.
0.01	0.1	Eaten through at water-line: lower part covered with purple "varnish" but unattacked below it.
0.003	0.1	Creepage above water-line and attack there: rest shows interference colours only.
0.001	0.1	Slight general brown stain, no attack.
Nil	0.1	" " " " "
KCl, M.	$\text{NaVO}_3$ , M.	
0.1	0.01	Adherent black coating, little attack.
0.1	0.1	Thin adherent dark coating, some interference colours and little attack.
0.01	0.1	Thin brownish-green protective coating.
0.001	0.1	Very slight edge corrosion: faces unchanged.
Nil	0.1	No attack.
KCl, M.	$\text{H}_2\text{O}_2$ , M.	
0.1	0.002	Normal corrosion as in plain KCl.
0.1	0.02	Attack in vertical streaks.
0.1	0.2	Almost general attack, very intense.
Nil	0.2	Slight attack at water-line and edge.

*Reaction between Ferrous Compounds and Chromates.*—Solutions containing  $\text{FeSO}_4$  and  $\text{NaOH}$  in equiv. proportion were mixed, and measured quantities of  $\text{K}_2\text{CrO}_4$  aq. added; the mixtures were shaken with air for 10 mins. and filtered. When  $\text{K}_2\text{CrO}_4$  had been added in excess of the amount needed to oxidise the ferrous iron completely to ferric, the filtrate was yellow; otherwise it was colourless; the ppt., dissolved in  $\text{HCl}$ , contained no ferrous iron. Thus the product is a mixture or solid solution of hydrated  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ , and not a spinel. Even when insufficient  $\text{K}_2\text{CrO}_4$  was added for complete oxidation, ferrous iron was absent from the ppt., probably indicating that chromate catalyses oxidation by atmospheric  $\text{O}$ ; for when no chromate was added, it was very difficult to remove the last traces of ferrous iron by shaking with air alone, although the greater portion of the ferrous compound was oxidised quickly. The mixed  $\text{Cr}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$  was more gelatinous than the  $\text{Fe}_2\text{O}_3$  obtained when oxidation was effected by air.

When  $\text{FeSO}_4$  was treated with  $\text{K}_2\text{CrO}_4$ , the whole of the  $\text{Fe}$  could be thrown down as a ppt. containing  $\text{Fe}^{+++}$ ,  $\text{Cr}^{+++}$ ,  $\text{OH}^-$ , and  $\text{CrO}_4^{--}$ , if chromate was added in excess of 1 mol.  $\text{K}_2\text{CrO}_4$  to 1 mol.  $\text{FeSO}_4$ . With less chromate, the ppt. also contained  $\text{SO}_4^{--}$ , but the  $\text{Fe}$  was completely pptd., provided that chromate was added in excess of 2 mols.  $\text{K}_2\text{CrO}_4$  to 3 mols.  $\text{FeSO}_4$ . Still less chromate failed to ppt. the  $\text{Fe}$  completely.

The basic salts in the ppt. yielded the hydroxides on boiling with  $\text{NaOH}$  aq. When  $\text{FeSO}_4$  and  $\text{K}_2\text{CrO}_4$  were mixed, and  $\text{NaOH}$  added in the amount required by the equation



the ppt. contained no  $\text{CrO}_4^{--}$  or  $\text{SO}_4^{--}$ , but only  $\text{Fe}^{+++}$  and  $\text{Cr}^{+++}$ . Thus the final product obtained from  $\text{FeSO}_4$ ,  $\text{K}_2\text{CrO}_4$ , and  $\text{NaOH}$  is the same, whether chromate or alkali is added first to the  $\text{Fe}$  salt.

Analogous expts. with  $\text{KMnO}_4$  and  $\text{NaVO}_3$  showed that, in absence of alkali,  $\text{Fe}$  is only partially pptd. even by large excess of these salts.

*Chromium in the Corrosion Product.*—Steel specimens were allowed to corrode in chloride-chromate solutions, adjusted to produce stage (b) (p. 2476). The membranous rust was removed, washed in hot  $\text{H}_2\text{O}$ , and dissolved in  $\text{HCl}$  aq.;  $\text{Na}_2\text{O}_2$  was added, and the liquid boiled, filtered, and tested with benzidine in  $\text{AcOH}$ .  $\text{Cr}$ , in the trivalent state only, was invariably present in the rust formed on steel corroding in such mixtures. Thus the secondary corrosion product produced in presence of chromate is a heterogeneous mixture or a solid solution of hydrated  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ .

*Chromium in the Protective Films.*—Steel specimens were treated in four ways: (1) Abraded, and immediately immersed for 24 hrs. in 0.67M- $\text{K}_2\text{CrO}_4$ . (2) Abraded, and immediately immersed for 24 hrs. in 0.67M- $\text{K}_2\text{CrO}_4$  containing 0.05M- $\text{KCl}$ . (3) and (4) As (1) and (2) but exposed to air for 24 hrs. between abrasion and immersion.

All the expts. were performed in triplicate. The specimens were thoroughly washed, and after trimming off all edges, the oxide film was stripped by the iodine method (Evans, J., 1927, 1020). It was thoroughly washed with hot  $\text{H}_2\text{O}$  on a filter, and dissolved in hot dil.  $\text{HCl}$  aq. The solution was oxidised with  $\text{Na}_2\text{O}_2$ , boiled, filtered, acidified with  $\text{AcOH}$ , evaporated to small bulk (2 c.c.), and tested for chromate with diphenylcarbazide (Stover, J. Amer. Chem. Soc., 1928, 50, 2363). Blank tests performed (a) on films stripped from

steel not treated in chromate, and (b) with the unoxidised solution of all the films from the chromate-treated specimens gave no indication of chromate. The stripped films contained Cr in the trivalent state alone; approximate colorimetric estimations in films stripped after treatments (1), (2), (3), and (4) indicated the  $\text{Cr}_2\text{O}_3$  contents as  $5 \times 10^{-8}$ ,  $1 \times 10^{-7}$ ,  $1 \times 10^{-8}$  and  $2 \times 10^{-8}$  g. per  $\text{cm}^2$  respectively. The film stripped from the rejected edges contained a greater proportion of  $\text{Cr}_2\text{O}_3$  than that from the corresponding main portions.

#### *Discussion.*

The results summarised in Table I show that chromate possesses powers of inhibiting corrosion by potassium chloride greatly superior to those of the other oxidising agents studied. Permanganate is comparatively useless; vanadate gives a degree of inhibition, but the mechanism is manifestly different, for thick visible layers of adherent secondary corrosion product are deposited on the metal. Hydrogen peroxide appears to accelerate corrosion under these conditions (see, however, Wieland and Franke, *Annalen*, 1929, 469, 257, for study of other conditions). Evidently oxidising properties do not necessarily involve inhibition, and the value of chromates is partly due to the fact that they will completely precipitate ferrous iron in the absence of alkali, and partly to the presence of chromic oxide in the protective film.

Owing to the small quantities involved, the chromium estimations in the film are approximate, but the relative order is not in doubt. The films produced when the specimens are immersed in chromate solution immediately after abrasion definitely contain more chromic oxide than those produced when 24 hours' exposure to air is allowed before immersion—a clear indication that in the former case the original ferric oxide film is less perfect and requires more repair. The abnormally high chromic oxide content of the edge portions is likewise to be attributed to imperfections in the natural film, due to stresses and physical defects in the metal. Again, the presence of chloride produces films with a higher chromic oxide content than those produced in absence of chloride. This accords with the well-known action of chlorides in penetrating the oxide film; breakdown by chloride will involve subsequent repair by chromate, and consequently a film containing more chromic oxide.

It has been found (Evans and Stockdale, J., 1929, 2651) that the amount of ferric oxide in films produced on abraded iron by air and chromate exposure is of the order of  $10^{-5}$  g. per sq. cm. The chromic oxide content of films "repaired" by chromate has been shown to be only 0.1—1.0% of this amount, which indicates that the function of the chromic oxide is to assist in the filling up of small gaps in the original ferric oxide film. An analogy is provided by the film

produced on aluminium by phosphate treatment; this contains only small and variable amounts of phosphate (Bannister, J., 1928, 3166); presumably, the aluminium phosphate serves to repair the places where the "natural" oxide film is weakest, the main part of the film remaining unchanged.

Cases are known, however, where a chromium compound forms the main material of a protective coat. Sutton and Le Brocq (*J. Inst. Met.*, 1931, 46, 53) found that the khaki-brown film produced on magnesium by a solution containing potassium dichromate, sodium hydroxide, and potash alum gave the tests for chromic chromate. Other chromium compounds may also occur: a magnesium alloy containing manganese yielded a darker film, thought to contain manganous chromate. Bengough and Whitby (*ibid.*, 1932, 48, 148), after testing the effect of 500 solutions on the subsequent behaviour of magnesium, report that most of those having protective action contained a chromate. During the present work, it was found that iron or steel placed in chromic acid solution containing small amounts of sulphuric acid may undergo a certain amount of corrosion, and then become covered with a thick adherent layer of fairly protective corrosion product containing a large proportion of trivalent chromium. In such cases the original air-formed film is evidently broken down, and protection is required by the entire surface, and not only at small gaps in an air-formed film. Thus a high chromium content is to be expected.

The resistant properties of chromium and its alloys can be explained on the theory of Pilling and Bedworth (*ibid.*, 1923, 29, 529), which predicts protection only where the ratio of the natural volume of an oxide to the volume of metal contained in it exceeds unity; this ratio, which is 0.84 for magnesium, 1.59 for zinc, 2.06 for iron, and 2.07 for manganese, is as high as 3.92 for chromium. These figures refer to anhydrous oxides; the hydrated oxides are still more voluminous. But inhibition by soluble chromates will be assisted by the fact that any iron commencing to pass into solution at weak points in the air-formed film will be immediately precipitated quite irrespective of the cathodically formed alkali. Even if precipitation by alkali at the weak points is considered to be instantaneous, it is evident that two oxides produced at a weak point will have more effective plugging action than one. Probably the gelatinous character of the ferric-chromic hydrated oxide mixture is favourable to its plugging properties; certainly any *granular* magnetite (sometimes present in the secondary corrosion product, where oxygen is the only oxidising agent present) would militate against protection (see Roetheli and Brown, *Ind. Eng. Chem.*, 1931, 23, 1010; Bengough, Lee, and Wormwell, *Proc. Roy.*

*Soc.*, A, 1932, **131**, 312); anhydrous magnetite, when once formed, is stable against dissolved oxygen.

*Summary and Conclusions.*

The film produced during inhibition of corrosion with chromate is found to contain small amounts of chromic oxide. The anti-corrosive properties of potassium chromate are ascribed to the plugging of weak points in the primary film with a mixture of hydrated chromic and ferric oxides, the main part remaining as ferric oxide. Five causes may contribute to the unique value of chromates as inhibitors. (1) Chromates are oxidising depolarisers, and allow the production of the cathodic product, sodium hydroxide, so close to the anodic weak points as to precipitate any iron salts in physical contact in the metal. (2) Unlike most oxidising agents, chromates can precipitate the whole of any anodically formed ferrous salts *in situ* irrespective of help from cathodically formed alkali (compare the immunity of iron in sodium phosphate or lead in sodium sulphate). (3) Unlike the depolarising action of some oxidising agents, that of chromates involves precipitation of a second substance, hydrated chromic oxide. (4) The mixture of hydrated oxides has the gelatinous character which Roetheli's work indicates as favourable for protection. (5) Even an anhydrous mixture of chromic and ferric oxides is known to have exceptionally satisfactory protective properties (compare the corrosion-resistance of chromium steel, where the primary film contains both oxides); mixtures of ferric oxide with the oxides of manganese or vanadium are not protective, nor is manganese or vanadium steel corrosion-resistant.

We thank Dr. J. J. Fox for a suggestion regarding analysis, and the Department of Scientific and Industrial Research for a grant.

[Received, August 8th, 1932.]

---