

1,640 cm^{-1} band and showed that at 150°C, and at a pressure of 3×10^{-5} mm of mercury, the spectrum showed an absorption apparently equivalent to the background absorption for annealed silica; similar high-temperature treatment has also been found necessary completely to remove the band at 3,660 cm^{-1} . We have compared the spectra of untreated, treated and deuterated silica with ordinate expansion in some cases, and have observed that both the small residual band at 3,660 cm^{-1} (seen clearly in Fig. 2) and the band at 1,640 cm^{-1} (sharply defined in all spectra) are completely unaffected by the deuterium exchange. Although some contribution to the 1,640 cm^{-1} band is undoubtedly due to the harmonic of the SiO vibration, we propose from this evidence that both bands are associated with hydroxyl groups 'trapped' within capillaries or cracks and, therefore, unable to react either with quaternary ammonium compounds or with deuterium oxide.

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Inhibition of Corrosion of Copper in Chromic Acid

CORROSION of copper is inhibited in 0.1 N chromic acid of pH 1.6, a loss of 10 mg/dm^2 and no change in appearance is observed after four weeks' immersion. On the other hand, corrosion is significant in sulphuric acid of this pH, and a loss of 150 mg/dm^2 is recorded after an identical period of immersion. This communication describes experiments designed to obtain a fuller understanding of the mechanism by which chromate inhibits the corrosion of copper.

(1) Measurements of electrode potential and film thickness were made on copper chemically polished and left for 3 days in a desiccator over calcium chloride. As shown by the electrometric reduction technique devised earlier¹, specimens treated in this way are covered by a film made up of 14 Å of cuprous oxide and an unidentifiable mixture of copper salts requiring 0.25 mC/cm^2 for reduction.

The results in Table 1 were obtained. These show that the protective power of the oxide film in copper is less in sulphuric acid than in chromic acid.

Table 1

(a) Electrode potential measurements (hydrogen scale)

(i) Copper in 0.1 N sulphuric acid	
On immersion	+0.18 V
After 43 h	+0.20 V
(ii) Copper in 0.1 N chromic acid	
On immersion	+0.65 V
After 43 h	+0.68 V

(b) Oxide film thickness (calculated from a.c. bridge measurements at 2,000 c/s using a dielectric constant of 10.5 for cuprous oxide (ref. 2),

- (i) In 0.1 N sulphuric acid the apparent film thickness (or approximate thickness of the coherent section of the oxide film adjacent to the metal surface) decreased from 8.0 Å on immersion to ≤ 5.0 Å after 43 h.
- (ii) In 0.1 N chromic acid the apparent film thickness increased from 22 Å on immersion to 32 Å after 43 h.

(2) An electrometric technique¹ was used to measure film thicknesses on copper which had been stored three days in a desiccator after a treatment comprising chemical polishing³ followed by electrochemical reduction of the

oxide. The cuprous oxide film on the copper surface was ≤ 3.0 Å immediately after this treatment, which increased to 6.0 Å after three days in the desiccator and to 16.0 Å after a further 43 h. Specimens were immersed in test solutions after three days in a desiccator, and left in the solution for 43 h. On removal from the test solution, these specimens were washed with distilled water, rinsed in acetone, and placed in the electrometric cell. The specimens were afterwards immersed in deaerated solution and the nature and thickness of the oxide film were determined (Table 2).

Table 2

- (a) In 0.1 N sulphuric acid, the cuprous oxide film after 43 h immersion was 38 Å thick.
- (b) In 0.1 N chromic acid, the film after 43 h immersion was 17 Å thick and no evidence of irreversible adsorption of chromate was obtained.

The results showed the total film thickness to be greater after immersion in sulphuric acid than in chromic acid; however, a.c. bridge measurements indicated that the film thickness decreased in the former solution. Thus it is evident that the film formed in sulphuric acid is porous, and the a.c. bridge measurements give an indication of the thickness of the coherent or non-porous section of the oxide film.

(3) Measurements of rates of solution of copper from bulk oxide, and oxide-covered copper, were compared and the results are shown in Table 3. Although the anion did not have any significant effect on the rate of solution of bulk oxide, the rate of solution of oxide from the metal surface was markedly decreased in chromic acid.

Table 3

	1 min	1 h	24 h
Concentration of copper, g.ion/l. dissolved from bulk cuprous oxide in 0.1 N H_2SO_4	—	4×10^{-3}	7×10^{-2}
Concentration of copper, g.ion/l. dissolved from bulk cuprous oxide in 0.1 N H_2CrO_4	—	10^{-2}	6×10^{-2}
Concentration of copper, g.ion dissolved from 90 cm^2 in 0.1 N H_2SO_4	3.1×10^{-5}	1.3×10^{-4}	10^{-3}
Concentration of copper, g.ion dissolved from 90 cm^2 copper in 0.1 N H_2CrO_4	3.5×10^{-5}	4.3×10^{-5}	6.4×10^{-5}

These three sets of experiments show that the effect of chromate on copper is to lower the chemical reactivity of the oxide film. The electrometric investigations of copper which had been immersed in chromate solution revealed no evidence of significant irreversible adsorption of chromate. However, when copper was immersed in chromic acid with a ratio of 2.2 ml. solution to 1 cm^2 of metal surface for 1 h, the oxide film stripped from the metal in a mixture of 10 ml. concentrated hydrochloric acid and 10 ml. 1:10 hydrogen peroxide made up to 100 ml. with washings from the specimen and the solution analysed, 2.5×10^{-5} g.ion of chromium was present. These results indicate that chromic ions formed by local electrochemical action had entered the oxide lattice to form a mixed cuprous chromic oxide having a lower chemical activity than the bulk cuprous oxide. It is considered that lowering the chemical activity of the oxide film is the major factor in inhibiting the corrosion of copper in chromic acid.

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Effect of Environment on the Orientation of the Nitrate Ions in Crystals

A ROTATIONAL or orientational disorder at room temperature in the arrangement of the nitrate ions has been observed in the crystalline lattices of a number of co-ordination compounds¹⁻⁴, although no one has so far offered any explanation for this phenomenon. The factors