

must exist between the metal and the pendulum bearing. Except at the point of zero charge, excess ions of one sign exist in the double layer and mutually repel each other, thus resisting compression increasingly with increasing departure from the potential of zero charge. As the charge on the metal increases, the mean distance from the bearing surface to metal surface increases, thus reducing the attractive force between the surfaces (or, effectively, the load of one surface on the other), and so diminishing the friction. Hence, μ is greatest when zero charge exists on the metal surface, and the potential at this point thus coincides with the $\frac{1}{a} \frac{da}{dt}$ -potential maximum.

It was suggested by Barker⁸ that the chief features of the friction-potential relations of platinum are due to the adsorption of oxygen and hydrogen. Bowden and Young⁹ later advanced a dual explanation in which effects due to the electrical double-layer are superimposed on effects due to adsorbed gases. That adsorbed gases are not always necessary to explain the effects of potential on friction is shown by the results for amalgamated copper where, for the potential range studied, adsorbed oxygen is absent and the adsorption of hydrogen is very small.

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Nov. 11.

¹ Rehbinder and Wenstrom, *Acta Physicochim.*, **19**, 36 (1944); *Doklady Akad. Nauk.*, **68**, 329 (1949).

² Rozhanski, *Zhurn. Tekn. Fis.*, **19**, 1056 (1949).

³ Grahame, Technical Report, U.S. Office of Naval Research, **2**, 19 (1950).

⁴ Frumkin and Gorodetskaya, *Z. phys. Chem.*, **136**, 215 (1928).

⁵ Gorodetskaya and Kabanov, *Phys. Z. Sowjet.*, **5**, 418 (1934).

⁶ Bockris and Azzam, *Trans. Farad. Soc.*, **48**, 145 (1952).

⁷ Karpachev and Stromberg, *Acta Physicochim.*, **12**, 523 (1940).

⁸ Barker, Dissertation, Cambridge (1947).

⁹ Bowden and Young, *Research*, **3**, 235 (1950).

Mechanism of Electropolishing

Electropolishing in molten salts. I have found that gold, platinum and palladium may be anodically polished using pure ('Analar') molten potassium chloride or sodium chloride as electrolyte. With palladium electrodes of about 1 cm.² area and 2 cm. apart at about 950° C., etching occurred at low current-density, but gave place to polishing at about 1 amp./cm.² (calculated on the inner faces only) and 3 volts potential difference. For gold at 970° C. and platinum at 1,020° C., using a 3-cm. diameter nickel crucible as cathode, there appeared to be no clearly defined lower limit to the polishing conditions, but polishing was observed at and above 0.15 amp./cm. and a potential difference of 1.5 volts. Palladium was also polished in an enclosed system with hydrogen bubbling vigorously through the electrolyte around the anode.

'Baser' metals than the three mentioned (for example, iron and copper) give less brilliant results, probably because they are attacked while cooling by the contents of the adhering electrolyte.

Conditions at polishing and etching anodic surfaces. The adsorptive conditions at polishing and etching copper surfaces have been directly compared in an arrangement consisting of a vertical cathode (1 cm. square) and a horizontal anode (1 cm. × 5 cm.) with

its long axis normal to the cathode and its tip 1 cm. from the centre. In 50/50 v/v phosphoric acid, it was possible to adjust the voltage (c. 1.2 V.) so as to produce three differing anodic bands simultaneously: (a) polish for 1 cm. from the tip; (b) an intermediate area; (c) etch on the remainder. When about 1 per cent of 'saturated' mercuric nitrate solution was included in the electrolyte, amalgamation took place on all except the polishing surface (a). Similarly, on anodes which had narrow, lightly amalgamated lines drawn along their lengths, mercury was removed in the polishing region but the lines broadened in the etch region. Bands similar to (a), (b) and (c) were produced in an electrolyte of 1 M CuSO₄ (at c. 3 V.) and behaved correspondingly towards mercuric ions, although the area (a) was matt and after a few minutes became covered with a dark brown deposit. In both phosphoric acid and copper sulphate, mercury droplets sprayed over the anode would not adhere readily to the area (a).

The experiments in molten electrolytes show clearly that electropolishing cannot be explained by postulating layers of oxide, hydroxide, etc., on the anode¹, for in this case the substances corresponding to oxides would be chlorides of the metals concerned, and under the conditions of the experiments the lattices of the chlorides of gold, platinum and palladium could not exist. The possibility of oxide films due to dissolved oxygen is ruled out by the experiment in hydrogen and by the observation that in all cases polishing could be obtained at temperatures well above those at which oxide could survive. Similarly, it is concluded from the behaviour of copper anodes towards mercuric ions in aqueous solutions that the non-adherence of mercury droplets to a polishing surface, reported by Hoar and Farthing², is due not to oxide films but to failure to establish a contact-adsorbed film of mercury at the relatively high current-density required for polishing. Further, since the etch-forms and growth-forms of metal crystals are controlled by adsorption³, the observations indicate that at high current-density etch is inhibited because the formation of regularly adsorbed layers is prevented. Polishing should then follow automatically, since the electric field will be highest at projections. The matt surface of type (a) obtained in copper sulphate electrolyte is believed to be due to the formation of solid by-products in contact with the metal, since it resembles that of a copper single crystal which has been attacked by iodine vapour with the formation of solid cuprous iodide.

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Sept. 20.

¹ Hoar, T. P., and Mowat, J. A. S., *Nature*, **165**, 64 (1950).

² Hoar, T. P., and Farthing, T. W., *Nature*, **169**, 324 (1952).

³ Erdey-Gruz, T., *Z. phys. Chem.*, **A**, **172**, 157 (1935). Tamman, G., and Sartorius, F., *Z. anorg. allgem. Chem.*, **175**, 97 (1928). Gwathmey, A. T., and Benton, A. F., *J. Phys. Chem.*, **44**, 35 (1940). Rowland, P. R., *Nature*, **164**, 1091 (1949).

Origin of the Methyleneoxy Groups of the Alkaloid Protopine

THERE is a rapidly increasing body of evidence in the literature that all biological methylation processes, as well as many other 'single-carbon' biological syntheses, have a common pattern. It has been shown that the N-methyl groups of the alkaloids