

of the diffusion layer fall below a certain critical limit either by dilution or by rise of temperature. On the other hand, even if the diffusion layer is much reduced in thickness (e. g. using an anode rotating 16,000 R. P. M.) polishing is still possible as long as the diffusion layer remains highly viscous, though a much higher current-density is necessary.

Experiment¹ has shown that the diffusion layer consists of a saturated solution of anode dissolution products in the electrolyte used for polishing. In the case of copper in phosphoric acid, the salt which crystallizes out from the diffusion layer is the phosphate ($4\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$), which was identified by measurements on the electron diffraction pattern (fig. 2).

It appears that an electrolyte which produces a polishing effect must be a good solvent for the anode dissolution products to ensure a high viscosity of the diffusion layer. A poor solvent would be quickly saturated with the products of dissolution and the viscosity of the diffusion layer would not be very different from that of the bulk electrolyte. There is also the risk in this case of salt crystallizing out as an insoluble crust on the anode at moderate current densities and stifeling the levelling effect of the current.

The case of copper in phosphoric acid is typical of most electrolytic polishing processes. A different type, however, is exemplified by the electrolytic polishing of silver in cyanide medium. In this case, when the limiting current density is reached, the concentration of CN' at the anode surface falls to zero, and the maximum rate at which the anode can dissolve to form $[\text{Ag}(\text{CN})_2]$ ions is determined by the maximum rate at which the CN' ions diffuse to the anode from the bulk of the solution. Any attempt to increase the current density results in the formation on the anode of a brown film, which is shown by electron diffraction to be silver cyanide, and not oxide as originally believed by HEDGES². The onset of this film is marked by a rise in anode potential, after which a series of oscillations begins and the anode surface displays alternate brown and silver white flashes, during which it becomes more and more bright.

This brown cyanide film functions in place of the highly viscous diffusion layer. It does not conduct the electric current, but it has a fine pored structure. The local differences of electric field intensity corresponding to the non-homogeneities of the surface (fig. 1) will attract more CN' to the projections. As the film is soluble in presence of CN' , the total cross section of the pores over the projecting parts will be augmented³ (relative to the pore cross section of the recesses). Accordingly less resistance will be offered to the anions trying to penetrate the film at the projections to reach the silver metal surface. The net result will be higher rate of attack at the projections and a polishing effect.

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M. HALFAWY

Applied Physical Chemistry Laboratory, Institute of Chemical Technology, Farouk University Alexandria, Egypt, August 10, 1950.

¹ M. HALFAWY, Thesis London, 1948; Also Bull. Anal. C. N. R. S. 10, (1) (1949).

² E. S. HEDGES, J. Chem. Soc. 1533 (1926).

³ The film grows only thickness until equilibrium is reached between formation and dissolution by the electrolyte.

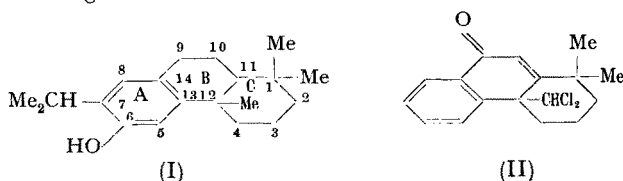
Zusammenfassung

Die vorliegende Theorie betrachtet die elektrolytische Polierung von Metallen als Resultat einer Anreicherung der Anionen an den Spitzen von Unebenheiten der Metalloberfläche. Die Anreicherung kommt dadurch zustande, daß diese Erhebungen eine besonders hohe elektrische Feldstärke aufweisen und deshalb die Anionen bevorzugt anziehen. Dabei sind die Anionen in den viskosen Schichten auf der Metalloberfläche nur wenig beweglich.

Diterpenes;

Preliminary Synthetical Experiments

The structure of ferruginol has been shown by degradation to be (I)¹, in which the nature of the ring-fusion B/C is thought to be *trans*².



This note is concerned with experiments directed toward the synthesis of (I) with *trans* fusion of rings B/C.

Ethyl γ -(4-methoxynaphthyl) butyrate on treatment with methyl magnesium iodide, followed by dehydration of the product, afforded Δ^2 -2-methyl-5-(4'-methoxynaphthyl)pentene, b. p. 132–137°C/0.03 mm, which on cyclisation with boron trifluoride in chloroform solution yielded 1:1-dimethyl-1:2:3:4-tetrahydro-9-methoxyphenanthrene, m. p. 59°C. Demethylation of the latter compound with hydrogen iodide furnished 1:1-dimethyl-1:2:3:4-tetrahydro-9-phenanthrol, m. p. 139°C. By an application of the Reimer-Tiemann reaction³ to 1:1-dimethyl-1:2:3:4-tetrahydro-9-phenanthrol, a dichloromethyl group was introduced into the angular position (C_{12}) to give 1:1-dimethyl-9-keto-12-dichloromethyl-1:2:3:4:9:12-hexahydrophenanthrene (II), m. p. 124°C, in which the 10:11-double bond provides a possible means of stereochemical control of the fusion of rings B/C. Experiments on the hydrogenation of (II) and of the simpler model substances 1-methyl-1-dichloromethyl-2-keto-1:2-dihydronaphthalene, m. p. 66–67°C, and 1-methyl-1-dichloromethyl-4-keto-1:4-dihydronaphthalene, m. p. 106–107°C, derived from 1-methyl-2-naphthol and 1-methyl-4-naphthol respectively by the Reimer-Tiemann reaction, are in progress, and it is hoped that the method will be capable of extension to the synthesis of ferruginol itself. The use of the Reimer-Tiemann reaction to generate the gem-dimethyl group at C_1 is also under examination.

M. S. GIBSON

Dyson Perrins Laboratory, Oxford, October 30, 1950.

Zusammenfassung

Es wurde die Anwendung der Reimer-Tiemann-Reaktion zur Einführung von angularen Dichlormethylgruppen in Phenanthrenenderivate untersucht mit dem Ziel, Ferruginol synthetisch herzustellen.

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