

Polymer Deposits on Palladium Contacts

A POSSIBLE MECHANISM OF FORMATION AND INHIBITION

The formation of brown deposits of some kind of organic polymer on palladium contacts—and on contacts in other members of the platinum group of metals—when they are subjected to long continued rubbing together in air containing traces of certain organic vapours was first described by H. W. Hermance and T. F. Egan (1) of the Bell Telephone Laboratories nearly nine years ago. This unexpected phenomenon was reported after a long programme of investigation of the contamination of telephone relay contacts during all stages of manufacture and service. The brown deposit formed on palladium, platinum, ruthenium, rhodium and their alloys, but only to a small extent on gold and not at all on silver. Its occurrence required mechanical but not electrical operation of the contacts; arcing in fact appeared to destroy the deposits. Formation of the deposit was accompanied by a lubricating effect; in the absence of organic vapours severe wear resulted, but during polymer production wear was negligible. In a specially prepared relay completely free from organic materials of construction and organic vapours no deposits appeared.

Further work led to the conclusion that the deposits consisted of complex mixtures of amorphous materials of very high molecular weight resulting from layers of the organic contaminants chemisorbed on the palladium surfaces, the catalytic activity of the metal being responsible, at least to some extent, for the polymerisation effect. On the other hand well-known catalyst "poisons" such as lead, arsenic, antimony and bismuth were not successful in inhibiting the reaction when alloyed with the palladium from which the contacts were made.

A further study of this problem has now been reported by S. W. Chaikin (2) of the Surface Chemistry Department, Stanford Research Institute, California, together with the postulation of a possible mechanism of formation.

It is accepted by this worker that the catalytic properties of the platinum metals are obviously important in polymer formation, but it is argued that a high energy process with little discrimination is acting in conjunction with the catalytic process. Such a process, he believes, may be related to the exo-electron effect in which a freshly disturbed metal surface emits electrons—the phenomenon first described by J. Kramer (3) of Braunschweig, who devised the name on the assumption that the energy supply for electron emission is provided by exothermal recrystallisation or relaxation processes—and in which a non-metallic surface film such as an adsorbed layer of organic material appears to be necessary. Chaikin's experimental work included the measurement of charged particle emission from specimens of gold, silver and palladium when rubbed gently together. The results were not reproducible, but showed that for all samples counting rates significantly above background were obtained, indicating that the Kramer effect is to be observed with noble metals for the surface treatment used. From this, Chaikin advances a mechanism based upon the disturbance of the metal surface under rubbing, the steady supply of exo-electrons available at the film—metal interface being able to react with a variety of catalytically formed compounds and intermediates at the interface and thus initiate further reactions. In other words, polymer formation is thought to result from combined

processes of catalysis and charged particle bombardment.

In a further series of experiments Chaikin sought to prevent polymer formation by finding suitable inhibitors to the reaction. Using a modification of a Bell Telephone Laboratories frictional polymer apparatus in which a loaded palladium stylus was caused to rub against a palladium plate in an atmosphere of benzene vapour, it was found that tetraethyl lead inhibited polymer formation although tetraethyl tin, dimethyl mercury and tetraphenyl lead were ineffective. Perhaps a more interesting result was obtained with a number of organic compounds containing iodine. Methylene iodide, propyl iodide, *n*-butyl iodide and iodobenzene, as well as iodine itself, inhibited polymer formation; iodoform and *p*-diiodobenzene did not, but their lack of effect is possibly due to their low vapour pressure.

This inhibiting activity is attributed to the involvement of free radicals in the polymer forming reaction—a possibility envisaged by

Hermance and Egan—since the successful compounds are known to be substances which terminate free radical chains and may well interfere in the course of the polymer reaction.

It is possible to speculate a little further on the usefulness of iodine compounds in this way, bearing in mind the recent studies of R. S. Owens, R. W. Roberts and their collaborators (4) at the General Electric Research Laboratory, Schenectady, on the function of iodine compounds in lubrication. Here the mechanism involved appears to be the reaction of iodine with the wearing metal surface to form a metal diiodide, a lamellar solid having a low shear strength in one plane.

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References

- 1 H. W. Hermance and T. F. Egan, *Bell System Tech. J.*, 1958, **37**, (3), 739-776; see also *Platinum Metals Rev.*, 1959, **3**, 19-21
- 2 S. W. Chaikin, *Wear*, 1967, **10**, 49-60
- 3 J. Kramer, *Z. Physik*, 1949, **125**, 739-756; 1950, **128**, 538-545; 1952, **133**, 629-646
- 4 R. S. Owens, R. W. Roberts and W. J. Barnes, *Wear*, 1966, **9**, 76-91

Sulphur-modified Platinum Catalysts for Fuel Cells

A number of aspects of the present state of fuel cell development were reviewed at a recent meeting held in Essen under the auspices of the Deutsche Gesellschaft für Flugwissenschaften and the Wissenschaftliche Gesellschaft für Luft-und Raumfahrt. As has been noted on numerous occasions, platinum metal electrocatalysts continue to be widely studied in many different reaction systems.

In a paper by H. Binder, A. Köhling and G. Sandstede of the Battelle Institut, Frankfurt, interesting news was given of the modification of Raney-type platinum electrocatalysts by the adsorption of a mono-layer of sulphur in the form of hydrogen sulphide. This is easily adsorbed on to a platinum surface and remains stable up to high electrode potentials in aqueous acidic electrolytes; oxidation to sulphur dioxide does not take place below potentials of 600 mV. Such sulphur-modified platinum catalysts showed exceptional activities in the electrochemical oxidation of carbon monoxide and formic acid to carbon dioxide. The experiments were carried out in 3N sulphuric acid, and using

carbon monoxide as fuel current densities of 200 mA/cm² at potentials around 250 mV and at temperatures of about 90°C were achieved. With formic acid these levels were attained at about 30°C. This was stated to be the first time that such current densities had been obtained with these fuels, since particularly strong polarisation with untreated platinum catalysts is generally observed.

Dr Ph. Dard of the Compagnie Française Thompson-Houston described a wide new range of fuel cell accessory components, including a high pressure hydrogen container made of glass fibre reinforced plastics. These components were developed for a range of about ten different fuel cell models intended for meteorological, television, aerospace and military applications; most of these will be fuelled by hydrogen and use an ion exchange membrane with platinum-catalysed electrodes on each side. Latest metal loadings have been as low as 8 to 10 mg/cm² of platinum, and complete fuel cells with outputs up to 12 kW have been constructed.

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