HOKKAIDO UNIVERSITY

Title	THE EFFECT OF CADMIUM ON THE ACTIVITY OF PLATINUM BLACK IN HYDROCARBON ELECTROOXIDATION
Author(s)	THACKER, Raymond
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 16(1), 35-43
Issue Date	1968
Doc URL	https://hdl.handle.net/2115/24847
Type	departmental bulletin paper
File Information	16(1)_P35-43.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

J. Res. Inst. Catalysis, Hokkaido Univ., Vol. 16, No. 1, pp. 35 to 43, (1968)

THE EFFECT OF CADMIUM ON THE ACTIVITY OF PLATINUM BLACK IN HYDROCARBON ELECTROOXIDATION

By

Raymond THACKER

Research Laboratories, General Motors Corporation
Warren, Michigan, U.S.A.

(Received October 27, 1967)

Abstract

The effect of cadmium on the activity of platinum black in hydrocarbon electrooxidation has been investigated. The platinum electrodeposits were prepared from 2.5% chloroplatinic acid solutions containing cadmium sulfate concentrations between 0.003 and 0.2% using a current density of 10 mA/cm² for 30 min. The Cd/Pt atomic ratio increases up to a concentration of adout 0.1%, whereafter it decreases with further increases of concentration. The roughness factor of the deposits and the degree of hydrocarbon oxidation vary in the same manner with Cd/Pt atomic ratio. The unsaturated hydrocarbons ethylene and propylene are more extensively oxidized than the saturated hydrocarbons ethane, propane, and *n*-butane for all values of the atomic ratio. It is shown that the degree of hydrocarbon oxidation increases proportionately with the roughness factor. The roughness factors of the deposits having Cd/Pt atomic ratios from 0 to 0.008 and from 0.008 to 0.05 decrease by 25 and 40%, respectively, in a two-week period.

1. Introduction

A study of the available literature reveals that the most active catalyst for the electrochemical oxidation of the gaseous hydrocarbons is finely divided platinum black admixed with a few per cent of ruthenium.[1] Up to a point the amount of catalyst used determines the rate at which a hydrocarbon is oxidized.[2] The question arises whether surface area is the sole criterion for electrochemical activity. In previous work[3] an attempt was made to find an answer to this question by investigating the nature of electrodeposited platinum blacks, containing different amounts of lead, in relation to their activity toward the electrooxidation of the five gases ethane, ethylene, propane, propylene, and *n*-butane. It was shown that the degree of hydrocarbon oxidation increases proportionately with real area, and that this effect tends to mask other factors,

such as lattice parameter, that might be important in electrooxidation reactions.

In continuation of this work, an investigation of the effect of cadmium on the nature and electrochemical activity of electrodeposited platinum blacks has been carried out. Cadmium was selected because, like lead, it has a profound effect on the appearance and lattice parameter of electrodeposited platinum black.[4]

2. Experimental

The electrodes used in this work for the electrochemical measurements consisted of platinum wires 1 cm long and 0.5 mm in diameter. They were coated with platinum black by electrodeposition from 2.5% chloroplatinic acid solution containing x% of cadmium sulfate, where x was varied between 0 and 0.2%. A current density of 10 mA/cm^2 was used, and the electrodes were plated for 60 min, during which time they were alternately anodized and cathodized for intervals of 1.5 min using a timer and reversal switch. For the photomicrographic examination, X-ray measurements, and cadmium content determinations, the deposits were prepared on platinum foils 1 cm^2 in area. The cells used for the preparation of the electrodes were described in a previous paper.[3] An all-Pyrex glass H-cell of conventional design was used for the electrochemical measurements. For the area determinations, nitrogen was bubbled through both compartments. For the electroactivity determinations, the appropriate hydrocarbon was bubbled through the working electrode compartment, and nitrogen was bubbled through the counterelectrode compartment. The cell was operated at 80°C by immersion in a water thermostat. The cleaning procedures used for the electrodes and cells before use, and the purification of the 5 M phosphoric acid electrolyte, were described in a previous paper.[3]

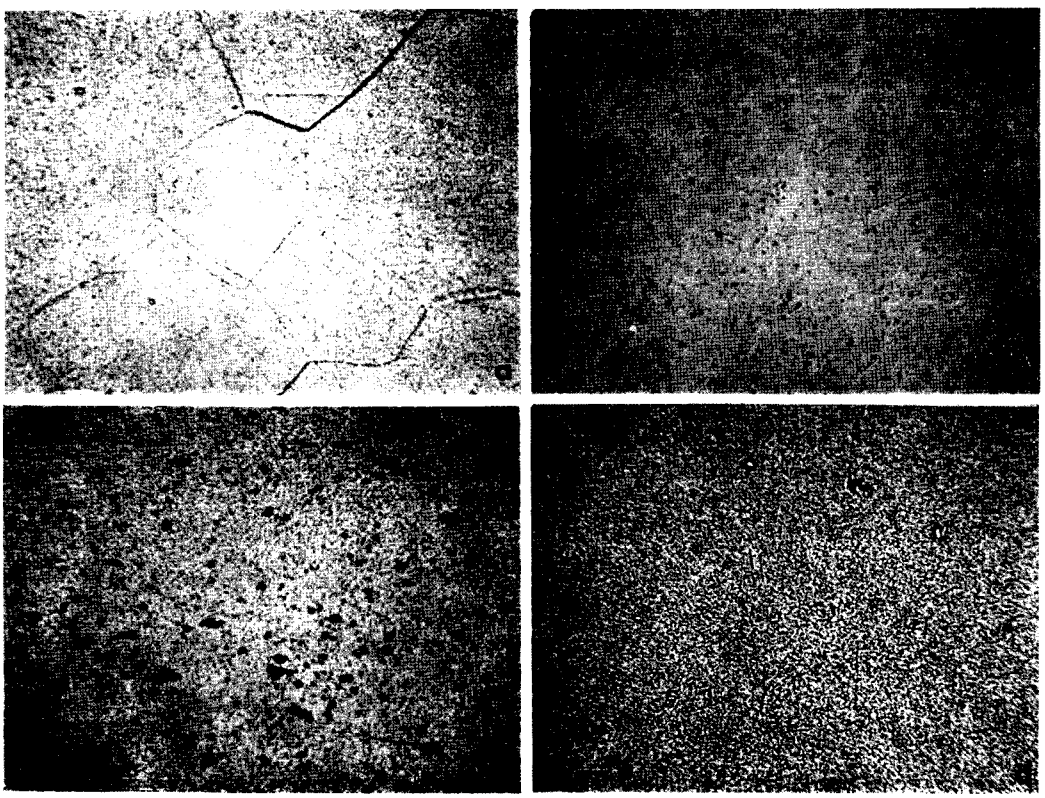
The sources and grades of the materials used were as follows: nitrogen—Matheson pre-purified grade; ethane, ethylene, propane, propylene, and *n*-butane—Matheson C.P. grade; chloroplatinic acid, cadmium sulfate, and phosphoric acid—Baker analytical reagent grade.

3. Results and Discussion

The cadmium sulfate concentrations and a description of the deposits are shown in the first two columns of Table 1. It will be seen that there was little variation in the appearance of the deposits up to a cadmium sulfate concentration of 0.075%. However, at a concentration of 0.1%, a bright deposit having a grey cast was obtained, and at a concentration of 0.2%,

a grey and nodular deposit was seen. In general the platinum foil supported deposits tended to be less uniform than those supported on platinum wires, presumably because of a less regular distribution of the current lines during the electrodeposition.

The surfaces of the deposits were examined in more detail with a Bausch and Lomb Dynazoom Metallograph using bright field illumination and magnification of 450×. The photomicrographs are shown in Fig. 1. In the absence of cadmium, Fig. 1 a, a coarse-grained deposit was obtained which did not block out the grain structure in the underlying basis metal. With 0.003% cadmium sulfate, Fig. 1 b, a finer grained deposit was observed, and in addition the deposit contained a number of nodular growths. The grain structure of the basis metal was faintly visible through the deposit. At the next higher concentration of cadmium sulfate, 0.01%, Fig. 1 c, a coarser-grained deposit was obtained, and the nodular growths, which were evident in Fig. 1 c, were larger and more numerous. With 0.05% cadmium sulfate, Fig. 1 d, the deposit was coarser than that in Fig. 1 c and contained only a few nodular growths. In



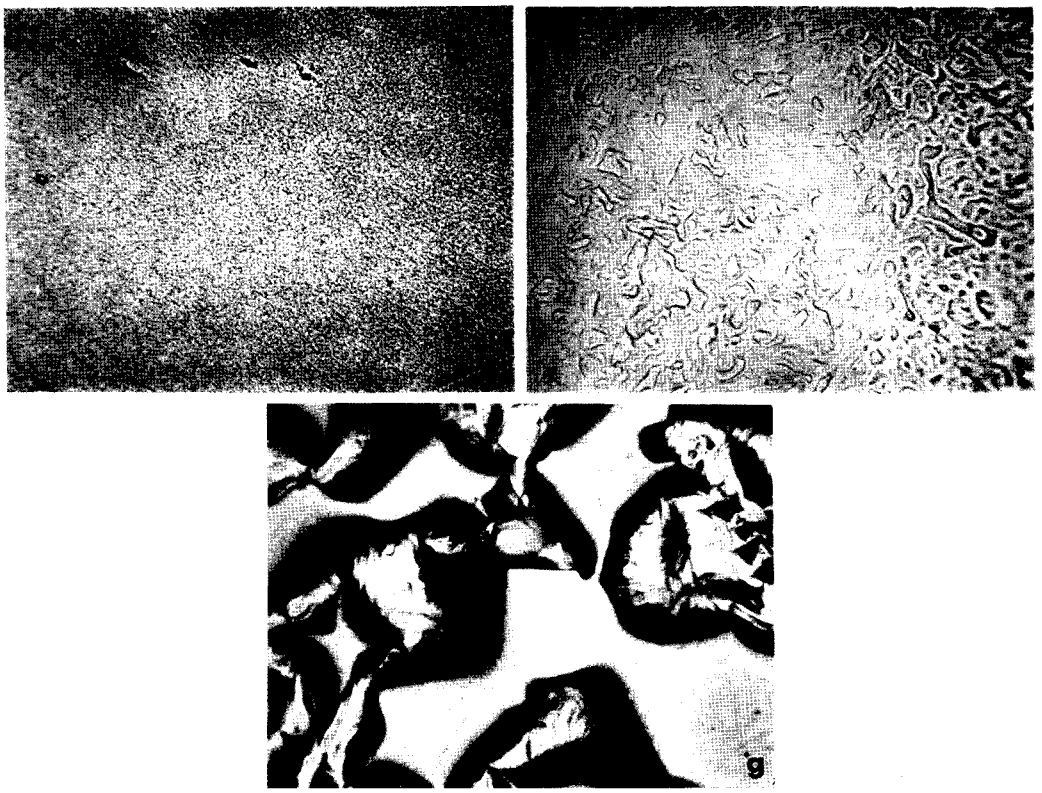


Fig. 1. Platinum black electrodeposits supported on smooth platinum. (Plating solution, 2.5% chloroplatinic acid+x% of cadmium sulfate at 25°C; current density, 10 mA/cm^2; time of plating, 60 min—30 min in the anodic and cathodic directions.) (a) $x=0$, (b) $x=0.003$%, (c) $x=0.01$%, (d) $x=0.05$%, (e) $x=0.075$%, (f) $x=0.1$% and (g) $x=0.2$%. Magnification 405 ×.

Fig. 1e, where the cadmium sulfate concentration was 0.075%, the deposit was finer than that in Fig. 1d; and in Fig. 1f, where the cadmium sulfate concentration was 0.1%, the irregular growth structure of the smooth metal was observed. With 0.2% cadmium sulfate, Fig. 1g, large nodules of the bright metal were seen, and a thin deposit on the basis metal was visible between them. It is interesting to note that cadmium can be used as a brightener in nickel deposition.[5] The coulombic efficiency for the deposits was about 35%, as shown in the third column of Table 1.

The deposits prepared by BIANCHI,[4] although having a similar appearance to those described here, were probably different in nature because he used a lower concentration of chloroplatinic acid solution (0.1%) and a considerably

TABLE 1 Properties of Platinum Black Electrodeposits

Cadmium Sulfate Concentration in Plating Solution (%)	Appearance of Deposits	Coulombic Efficiency (%)	Cd/Pt Atomic Ratio	Roughness Factor	
				Immediately After Preparation	After Two Weeks
0	Grey, compact		0	344	155
0.003	Grey	33	0.00245	362	262
0.01	Greyish black	33	0.00683	360	269
0.05	Greyish black	37	0.0297	340	224
0.075	Greyish, smoother	36	0.0462	285	158
0.1	Bright, grey cast	37	0.0508	300	213
0.2	Grey and nodular over 2/3 electrode	27	0.034	306	182

larger current density (625 mA/cm^2). His current efficiency was about 3%. It was shown in the present work that current densities greater than 10 mA/cm^2 led to much gassing and a finer deposit which tended to appear in the

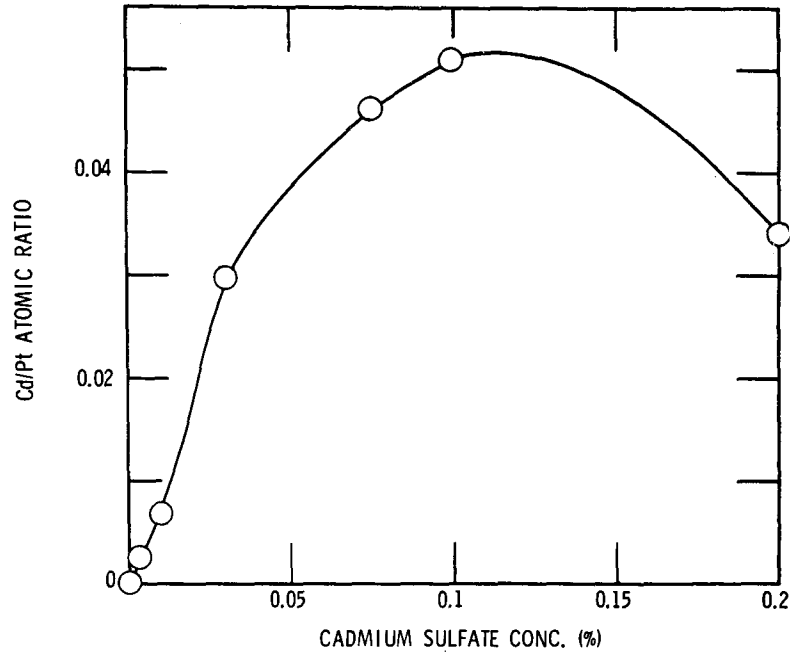


Fig. 2. Cd/Pt atomic ratio of electrodeposited platinum black prepared from 2.5% chloroplatinic acid solutions containing different cadmium sulfate concentrations.

electrolyte as a colloidal suspension. HACKERMAN has shown that variations in the nature of electrodeposited platinum black can result from changes in concentration and current density.[6]

The cadmium content of the deposits was determined by atomic absorption analysis. The Cd/Pt atomic ratios were calculated from the analytical data and are shown in the fourth column of Table 1. The plot of this ratio *versus* concentration of cadmium sulfate in the plating solution is shown in Fig. 2. It will be seen that the curve is almost parabolic, the maximum being between a concentration of 0.075 and 0.15%.

X-ray diffraction analysis of the deposits indicated that there was insufficient cadmium present to cause a measurable change in the lattice parameter. The deposit having an atomic ratio of 0.0025 showed only a few weak

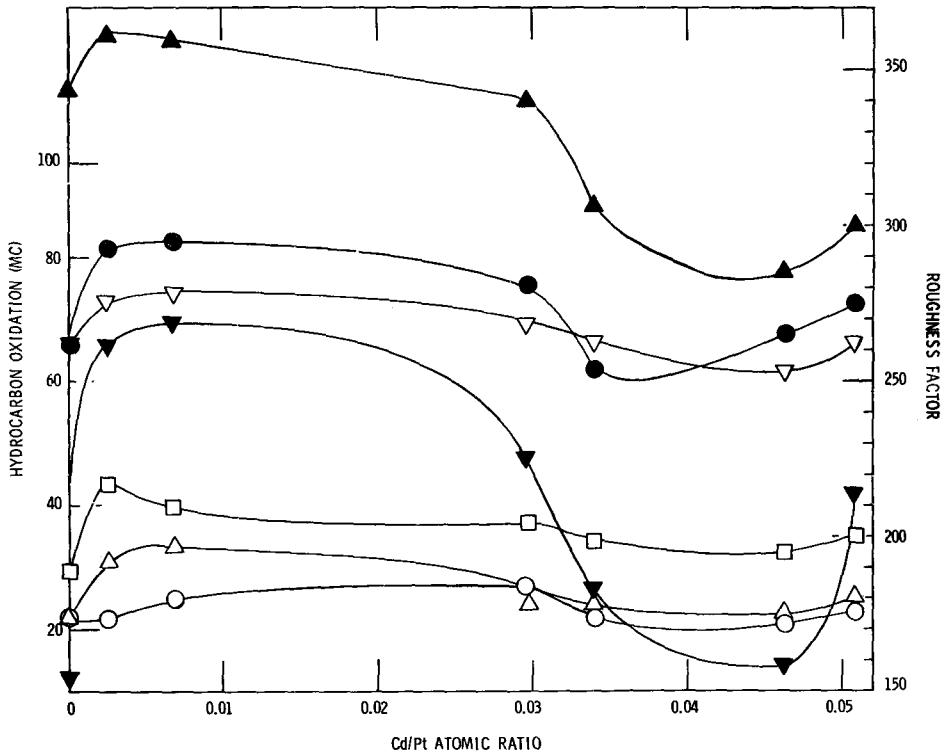


Fig. 3. Curves showing the variation of degree of hydrocarbon oxidation (5 M H_3PO_4, 80°C) and roughness factor with Cd/Pt atomic ratio. Roughness factor: ▲–immediately after preparation of the deposits; ▼–after two weeks. Degree of hydrocarbon oxidation: ethane, □; propane, ○; *n*-butane, △; ethylene, ▽; and propylene, ●.

platinum lines, whereas the deposits having atomic ratios of 0.0068, 0.0297, 0.0462, and 0.0508 gave normal diffraction lines for the elemental metal. The deposit which had an atomic ratio of 0.034 gave broad diffraction lines indicative of a fine crystallite size.

The area of the deposits was determined from the charge required to form a monolayer of oxygen atoms on the surface. A triangular voltage sweep (sweep rate 20 mV/sec) was applied potentiostatically to the electrode which was immersed in nitrogen stirred 5 M phosphoric acid at 80°C.[7,8] The trace produced contained an oxidation peak at 1.08 *versus* NHE (normal hydrogen electrode) which results from the formation of a monolayer of oxygen atoms on the electrode surface. The real area of the electrode was calculated from the area under this peak. It was assumed that there is one oxygen atom per surface platinum atom and that there are 1.6×10^{15} sites per

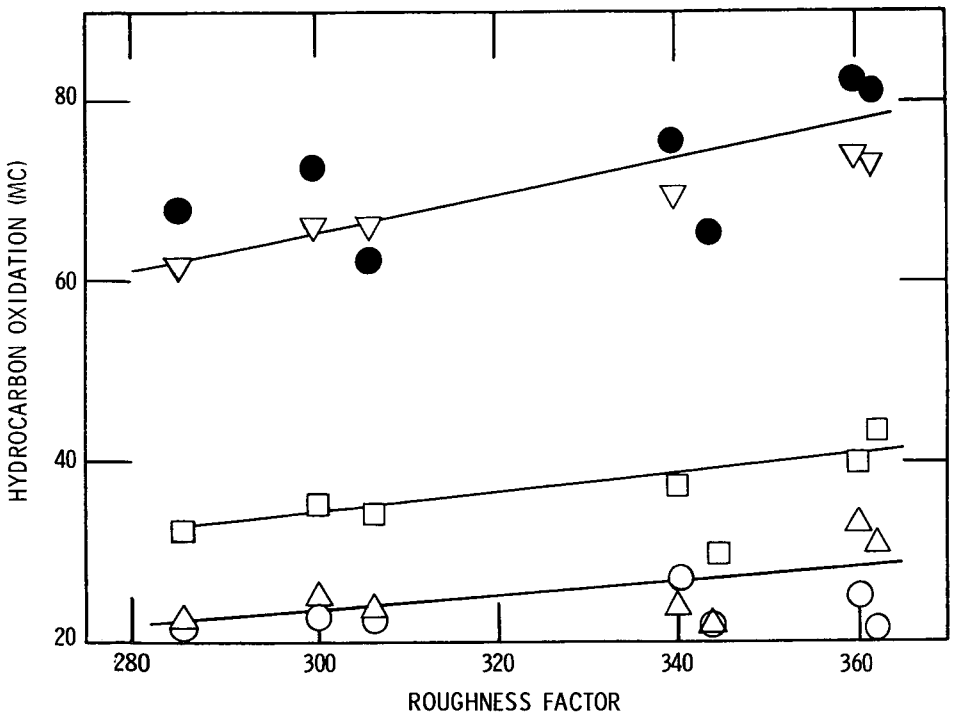


Fig. 4. Hydrocarbon oxidation (5 M H_3PO_4, 80°C) on electrodeposited platinum black prepared from 2.5% chloroplatinic acid solutions containing different cadmium sulfate concentrations. Variation with roughness factor as determined immediately after preparation of the deposits. Ethane, □; propane, ○; *n*-butane, △; ethylene, ▽; and propylene, ●.

square centimeter.[3] Measurements were made immediately after making the deposits and after a two-week period. During this period the electrochemical activity determinations were carried out. The roughness factors (real area per geometric area of 1 cm^2) on the two occasions are shown in the last two columns of Table 1.

In Fig. 3 is shown the plot of roughness factor *versus* Cd/Pt atomic ratio. The roughness factors determined soon after making the deposits are shown by the filled triangles, and the values determined after two weeks are shown by the filled inverted triangles. It will be seen that the two curves have essentially the same shape and that the one determined after two weeks lies below the one that was determined immediately after making the deposits. The decrease in roughness factor in the two-week interval was about 25% for the deposits having Cd/Pt atomic ratios of 0 to 0.008 and was 40% for the deposits having higher atomic ratios. In previous work[9] it was shown that the area of electrodeposited platinum black can diminish under certain circumstances by as much as 50%.

The electrochemical activity of the several deposits toward the five hydro-

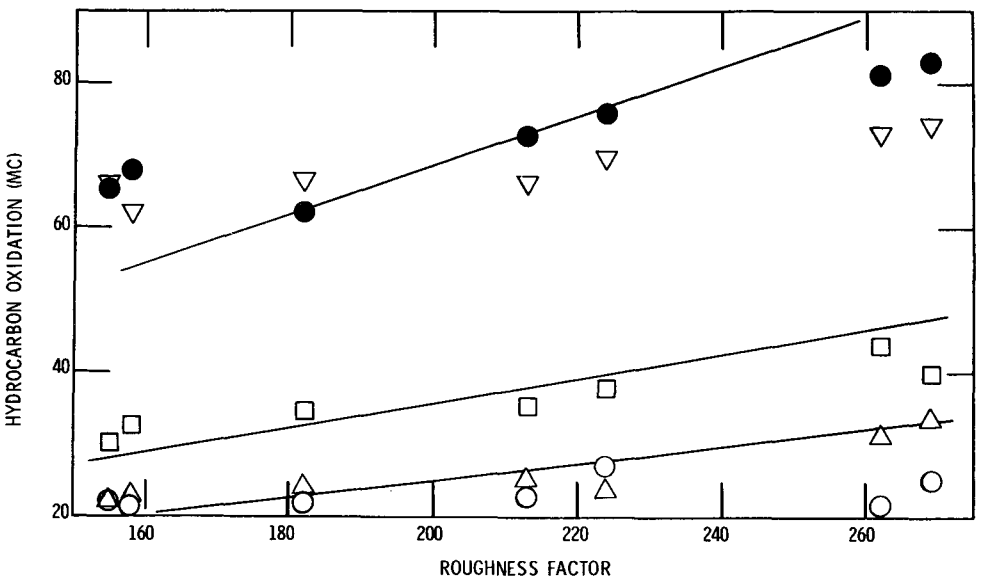


Fig. 5. Hydrocarbon oxidation (5 M H_3PO_4, 80°C) on electrodeposited platinum black prepared from 2.5% chloroplatinic acid solutions containing different cadmium sulfate concentrations. Variation with roughness factor as determined after a two-week interval. Ethane, □; propane, ○; *n*-butane, △; ethylene, ▽; and propylene, ●.

carbon gases ethane, ethylene, propane, propylene, anh *n*-butane was determined using the triangular sweep method.[7,8] The procedure used was described before.[3] The area under the oxidation peaks for the hydrocarbons, in millicoulombs (mc), was used as a measure of the electrode activity.

In Fig. 3 is shown the plot of hydrocarbon oxidation (area under the oxidation peaks) *versus* Cd/Pt atomic ratio. Two things are evident. First, ethylene and propylene are more extensively oxidized than ethane, propane, and *n*-butane for all values of the atomic ratio ; and second, the curves closely parallel those relating the roughness factor to the atomic ratio.

In Fig. 4 the degree of hydrocarbon oxidation is plotted against the roughness factors determined immediately after making the deposits, and in Fig. 5 the same hydrocarbon oxidation data are plotted against the roughness factors determined after two weeks. The solid lines shown in these figures were drawn such that they would pass through the origin and be the best fit with the experimental points. It is seen that the hydrocarbon oxidation, within experimental error, increases proportionately with the roughness factor and with, perhaps, the exception of ethylene and propylene in Fig. 5 decreases to zero at zero roughness factor.

The results described here are similar to those reported before[3] for lead-containing platinum black electrodeposits.

Acknowledgment

The author is grateful to Mr. A. H. JONES, Dr. J. L. JOHNSON, and Miss F. A. FORSTER of the Chemistry Department, Research Laboratories, General Motors Corporation, for carrying out the analytical work.

Literature

1) O. J. ADLHART and M. M. HARTWIG, ASTIA Rpt. AD 461362, April, 1965.
2) R. THACKER, Electrochem. Tech., **3**, 312 (1965).
3) R. THACKER. *Hydrocarbon Fuel Cell Technology*, B. S. BAKER, Editor, Academic Press, New York, 1965, p. 525.
4) G. BIANCHI, Annadi Di Chimica, **40**, 222 (1950).
5) E. B. SAUBESTRE, *Metal Finishing Guide Book*, N. HALL, Editor, Metals and Plastics Publications, Inc., Westwood, N. J., 1960, p. 376.
6) M. J. JONCICH and N. HACKERMAN, J. Electrochem. Soc., **111**, 1286 (1964).
7) J. L. GRIFFIN, J. P. HOARE and R. THACKER, G. M. Eng. J., **12**, 39 (1965).
8) F. G. WILL and C. A. KNORR, Z. Elektrochem., **64**, 258 (1960).
9) R. THACKER, Nature, **212**, 182 (1966).