TABLE 3

*g* VALUES OF LINES ATTRIBUTED TO FREE ELECTRONS AND/OR ADSORBED OXYGEN SPECIES[a]

| Sequential treatments | Davison Eta | Kaiser XA 331 | Harshaw 0104 | High-purity $\gamma$ alumina |
|---|---|---|---|---|
| Air | 2.034 ± 0.002 | — | — | — |
| | 2.001 ± 0.002 | — | — | — |
| | 1.967 ± 0.002 | — | — | — |
| $10^{-5}$ Torr, 500°C<br>330 Torr $H_2$, 500°C<br>$10^{-5}$ Torr, 500°C | 2.003 ± 0.002 | 2.003 ± 0.002 | 2.003 ± 0.002 | 2.003 ± 0.002 |
| Air, 500°C | 2.034 ± 0.002 | — | — | — |
| | 2.001 ± 0.002 | — | — | — |
| | 1.967 ± 0.002 | — | — | — |

[a] *g* values measured at room temperature.

fine structure points to a mobile species of charge carrier. Kazanskii *et al.* (*7*) have also assigned a line with $g = 2.002$ to free electrons captured in the conduction band.

A relation seems to exist between impurity content (as measured by the broad absorption) and the presence of the $g = 2.003$ signal. Introduction of extraneous cations will, of course, help to establish color centers and give semiconducting properties to the alumina.

In conclusion, we attribute the broad lines to impurities and not to absorbed oxygen species. Impurities may also be responsible for the broad line found in palladium-alumina catalysts (*1*). The narrow line with $g = 2.003$ is thought to be due to mobile electrons.

These results illustrate spectra that may arise directly or indirectly from impurities in, or from, high-temperature evacuation of aluminas.

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# Infrared Emission Spectra of Surfaces—An Interferometric Approach

Techniques for measuring infrared emission spectra of solid surfaces have recently been described (*1*). Conventional spectrometers were employed, and useful emission spectra were obtained. However, in order to obtain enough emitted radiation to operate the instruments, the sample surfaces had to be heated at least to 100°. This limited the utility of the emission method, and prompted the present study to explore the feasibility of measuring infrared emission spectra of surfaces near room temperature. Such measurements were possible.

The low emittance of surfaces at ambient temperatures implied that drastic instrument modifications and improvements would have to be made in order to measure low-temperature emission spectra with conventional dispersion spectrometers. In order to circumvent this, the present approach involving interference spectroscopy was attempted. An interference spectrometer that had performed well during balloon and satellite flights for atmosphere measurements as well as for terrestrial observation of stellar spectra was used (*2–4*). The instrument, now incorporated in the Block Model 200 infrared interferometer spectrometer, (Block Engineering, Inc., Cambridge, Massachusetts) basically is a Michelson interferometer and is described elsewhere (*5*). The instrument was set to scan the range of 3 to 15 $\mu$ twice per second with a spectral resolution of 40 cm$^{-1}$. The detector temperature was about 30°. The ordinates of relative spectral emittance (RSE) of Fig. 1 are arbitrary and are displaced to prevent overlapping.

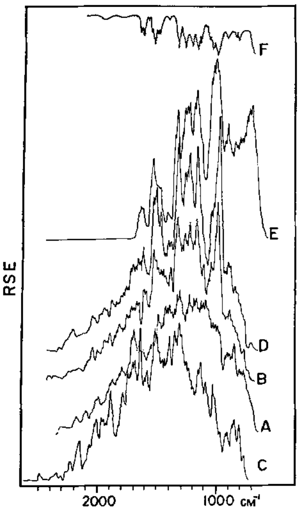

Fig. 1. Emission spectra of tricresyl phosphate on steel at 40°. Each emission spectrum represents the cumulative signals of 120 scans. A, polished steel surface; B, after tricresyl phosphate addition; C, after heating at 400°; D, after tricresyl phosphate addition; E, tricresyl phosphate on Irtran-2; F, absorption spectrum of tricresyl phosphate.

The results of some experiments with steel surfaces are shown in Fig. 1. Plot A is the emission at 40° of a steel surface that had been polished with steel wool. A thin coating of tricresyl phosphate was then applied and wiped off, and spectrum B was measured. The tricresyl phosphate used was a commercial mixture of isomers. The steel was then heated in air to 400° and after 5 min was cooled to 40°. Spectrum C was then obtained. The surface was again covered with tricresyl phosphate and wiped, and spectrum D was measured at 40°. Plot E is the emission spectrum of a thin layer of tricresyl phosphate on the surface of a plate of Irtran-2. Plot F is the absorption spectrum of a film of the tricresyl phosphate between Itran-2 plates, measured at room temperature with a Perkin-Elmer Model 521 spectrophotometer.

The band near 1300 cm$^{-1}$ of spectrum F corresponds to the $P{=}O$ vibration, and bands near 1190 and 1242 cm$^{-1}$ as well as weaker ones near 1030, 1040, and 1220 cm$^{-1}$ are assigned to the P–O–C linkage (*6*). The strong absorption band near 975 cm$^{-1}$ which also appears as the most intense emission band, close to an intense band near 980 cm$^{-1}$ found with many organic phosphorus compounds, is unfortunately not identified (*7*). Bellamy and Beecher have very tentatively associated the 980-cm$^{-1}$ band with the P–O stretching vibration of pentavalent phosphorous compounds (*8*).

Comparison of spectra A to F indicates that when tricresyl phosphate was applied to the steel surface, the emission bands of the tricresyl phosphate were superimposed on the emission of the metal so that structure similar to that of spectrum F appeared. The absence of new bands in spectrum B suggests that there was no significant reaction between the tricresyl phosphate and the steel surface at 40°. On heating the treated steel surface to 400°, however, some changes occurred. As shown by spectrum C, the P–O–C bands near 1190 and 1242 $cm^{-1}$ disappeared, as did the prominent 975-$cm^{-1}$ band. As spectrum C shows remnants of the 1300-$cm^{-1}$ band and of the 1500- and 1600-$cm^{-1}$ aromatic bands, this suggests that cleavage of the P–O–C linkage occurred in the tricresyl phosphate that remained on the surface and did not evaporate, some products containing P–O groups and aromatic systems remaining bound to the steel surface after the 400° heating.

The feasibility of measuring low-temperature emission spectra has been shown by these as well as by other experiments during which the infrared emission spectra of oleic acid on aluminum surfaces at 22° were measured with results (*1*) similar to those observed at higher temperatures. Numerous applications of the method to topics such as boundary lubrication or catalysis or biological systems readily come to mind. However, some difficulties remain. The resolution is relatively poor at present, but this particular failing is more than offset by the ability to observe spectra. The resolution problem, technological in origin and beyond the scope of the present discussion, is being improved. Also, the intensity–temperature behavior of emission bands, the total change in emission when a surface reaction occurs, the stability of a surface during long scanning periods and similar effects, some of which will be characteristic of the system examined, can be expected to cause some difficulty in the interpretation of emission data.

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# Nature of the Surface of a Platinum-Rhodium Alloy in Electrocatalysis

In recent years alloy surfaces have been used increasingly as electrode materials, particularly in connection with the oxidation of hydrocarbons (*1*). Little is known concerning the nature of the electrode surface of the catalyst. In this communication we report a phenomenon bearing on this for platinum-rhodium alloy catalysts.

In Figs. 1 and 2 are shown the steady state potential–log rate relationships for