

RECENT WORK ON ELECTRONIC PROPERTIES OF CARBONS AT THE UNIVERSITY OF BUFFALO*

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This is a review of results of work on the electronic properties of carbons performed at the University of Buffalo by several investigators. Studies of soft carbons have shown an anomalous variation of the Hall effect constant with heat treatment in the region of heat treatments around 1600–1900°C where puffing occurs, and the presence of negative magnetoresistance in the range of heat treatments 1700–2200°C (S. Mrozowski and A. Chaberski). The diamagnetic susceptibility of soft carbons has been studied as a function of temperature from liquid nitrogen to 1000°C and the susceptibility of residual bisulfate compounds of carbon has been investigated as a function of oxidation (H. T. Pinnick and P. Kiive). Microwave magnetic resonance absorption of electron spins has been studied as a function of heat treatment in soft and hard carbons from the raw state up to graphite (J. G. Castle, Jr. and D. Wobschall). Finally, quantitative investigations of the infrared response and of the absorption of pyrolyzed organic films have been carried out (J. Andrew).

At the first Carbon Conference a paper was presented by H. T. Pinnick on the work done at the University of Buffalo on the electronic properties of carbon up until that time¹. This included the electrical resistivity, Hall effect, thermoelectric effect, magnetic susceptibility, and infrared absorption of raw cokes. In the last two years, the work on the Hall effect and magnetic susceptibility has been extended as well as work on the infrared response of raw coke films, and much new data has been obtained on other electronic properties: the magnetoresistance and paramagnetic resonance. This paper will be mainly a presentation of results obtained since the first conference.

The recent work on the Hall effect has been done by S. Mrozowski and A. Chaberski². The samples used were made from

National Carbon baked soft carbon rods that were heat treated in a graphitizer furnace in the presence of a nitrogen atmosphere. Fig. 1 shows the Hall coefficient as a function of heat treatment, the highest temperature to which the sample had been previously heated. The two curves are for measurements taken at two different ambient temperatures—room temperature and liquid nitrogen temperature. The picture of the electronic nature of carbons, as deduced from the Hall effect and other electronic properties is as follows (see Fig. 9 in Reference 1): At low HT (heat treatment), around 1200°C, the carbon is a semiconductor with fairly large energy gap, and the Fermi level lies deep within the π -valence band, so deep that the electrons act, not like holes, but like electrons. The Hall effect is therefore relatively small and negative. With increasing HT , the Fermi level rises and the electrons soon begin to act like holes, so that the Hall coefficient becomes positive. With further increase of HT , the Fermi level continues to rise and the effective number of holes decreases, so

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¹ H. T. Pinnick, This volume, page 3.

² S. Mrozowski and A. Chaberski, *Phys. Rev.* **94**, 1427 (1954). A detailed paper is being prepared for publication in *Phys. Rev.*

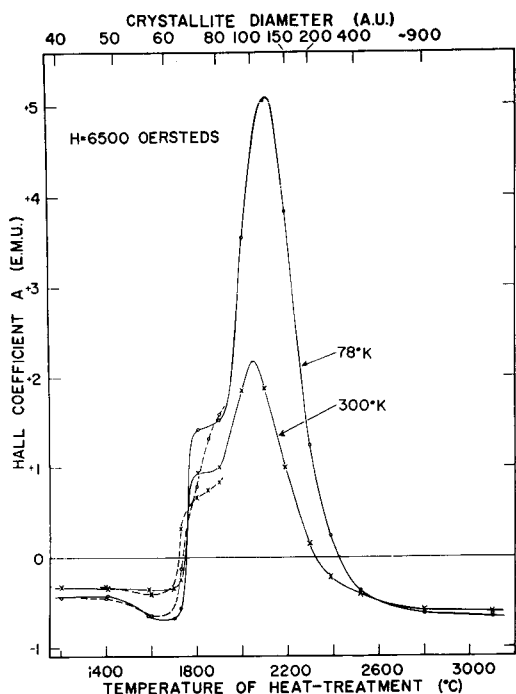


FIG. 1. Hall coefficient for a soft carbon vs. temperature of heat treatment.² The two curves correspond to values obtained at room temperature and at 78°K.

that the Hall coefficient becomes more positive. However, the energy gap also decreases as the temperature of HT is increased, so that eventually the energy of activation becomes of the order of kT and electrons start to be excited into the conduction band in large numbers. From here on the Hall coefficient begins to decrease with further increase in HT although the number of holes still decreases. This is because the number of electrons in the conduction band increases and because these electrons have greater mobility than the holes. The Hall coefficient soon turns negative even though the number of holes is larger than the number of electrons. For a HT of 3000°C the soft carbon becomes polycrystalline graphite, that is, an intrinsic semiconductor with zero (or nearly zero) energy gap. For such a semiconductor the number of electrons and holes are equal, but the Hall coefficient is

negative because of the greater mobility of the electrons.

The peak of the Hall curve occurs when the energy gap is of the order of kT and an appreciable number of electrons are thermally excited from the valence band to the conduction band. As seen in Fig. 1, the peak in the room temperature curve occurs at a lower HT than the peak in the liquid nitrogen temperature curve; that is, it occurs for a correspondingly larger energy of activation. The shift in the peak of the Hall curve with temperature can be considered as good evidence of the decrease of the energy of activation with increasing HT .

There are some other interesting features in the curve of the Hall coefficient. One can see in Fig. 1 a dip, a sharp rise, and then a hump in the Hall curve in the region between 1600°C and 1900°C which is in the

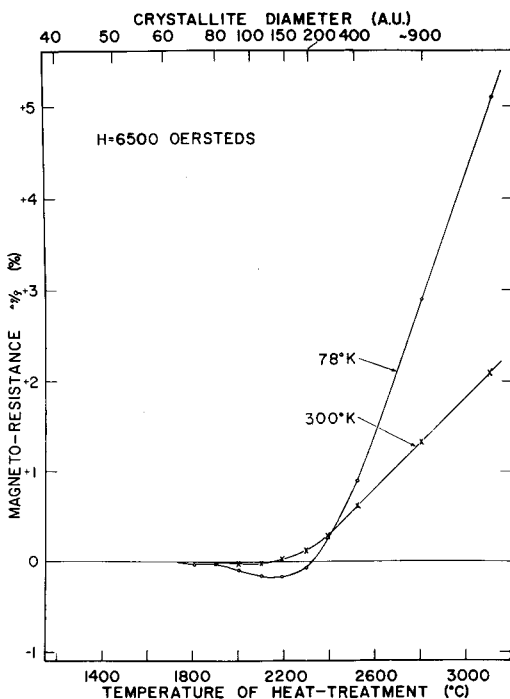


FIG. 2. Magnetoresistance for a soft carbon as a function of heat treatment for a field of 6500 gauss.² The two curves correspond to values obtained at room temperature and at 78°K.

region where puffing and the evolution of sulphur are known to occur during the graphitization process. One suspects therefore that this dip and hump in the curve are associated with the removal of impurities by heating. Samples heat treated within this region were heated at about 1000°C in an atmosphere of chlorine and some impurities were removed by this chlorination process. The Hall coefficient after chlorination changed slightly. The hump in the curve decreased, but did not disappear completely. Evidently chlorination does not remove the sulphur too well.

While investigating the Hall effect, Mrozowski and Chaberski also studied the magnetoresistance by measuring the change in the electrical resistance of a sample when placed in a magnetic field. Some of their results are shown in Fig. 2. $\Delta\rho/\rho$, the change in resistance divided by the resistance in the absence of a magnetic field, is plotted against HT . The magnetic field used here was 6500 gauss. When charges move in a magnetic field, the field exerts a force on the charges and they are deflected from what would be their field-free paths. One would expect, for that reason, that a magnetic field would always cause the resistance to increase. It is therefore surprising to find that for carbons over a narrow range of heat treatments, the resistance decreases in the magnetic field. This is a negative magnetoresistance. The effect is more pronounced at low temperatures; it seems significant that the minima of the two curves in Fig. 2 occur at approximately the same heat treatments as the peaks in the two Hall curves in Fig. 1. At room temperature the magnetoresistance varies as the 1.75 power of the magnetic field over the entire range of heat treatments. At liquid nitrogen temperature the exponent changes and is no longer constant over the whole range of field strengths; it is close to 2 at low magnetic fields and decreases gradually to 1.6 at high fields.

The magnetoresistance was also found to

depend on the relative orientation of crystallites with respect to the magnetic field. The magnetoresistance is greatest when the magnetic field is perpendicular to the graphitic planes of the crystallites. The samples used in the experiments were polycrystalline carbons obtained by cutting sections along and perpendicular to the axis of large extruded soft carbon rods, and the magnetoresistance was found to depend strongly on the orientations of the magnetic field and the current with respect to the axis of the extruded rod. The magnetoresistance can therefore be used as a very sensitive tool for the study of the degree of crystalline alignment.

Measurements have also been made of the magnetoresistance of some residual bisulfate compounds of carbons. The bisulfate ions act as acceptors, increasing the effective number of holes in the π -valence band. If a bisulfate compound with HT around 3000°C is prepared, the magnetoresistance decreases and continues to decrease as the ionic concentration is increased. For a carbon with slightly positive magnetoresistance, the addition of bisulfate ions causes the magnetoresistance to become negative. For a sample with slightly negative magnetoresistance, as the ionic concentration increases, the magnetoresistance first becomes more negative and then increases, tracing out something similar to the bottom of the curve in Fig. 2. In general, the addition of acceptor ions causes a change in the magnetoresistance which corresponds to a shift toward lower HT . This is additional evidence that the number of excess holes is higher for carbons heat treated to lower temperatures. The negative magnetoresistance seems to be in some way connected with the position of the Fermi level, but nothing more can be said about it since there is no theory at present which can explain the existence of a negative magnetoresistance.

A number of new results have been obtained in the last two years on the magnetic

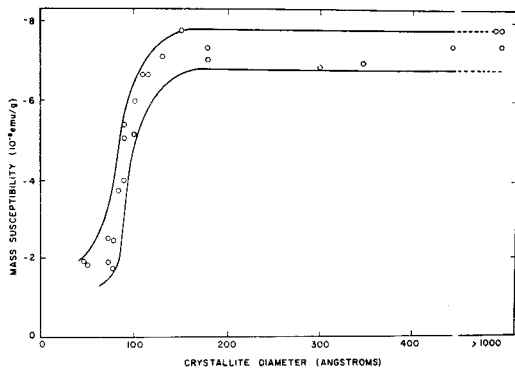


FIG. 3. Magnetic susceptibility vs. crystallite diameter for National Carbon rods and Thermax carbon black powders³.

susceptibility by H. T. Pinnick and P. Kiive^{3, 4}. Fig. 3 shows the diamagnetic susceptibility plotted as a function of crystallite size. The crystallite sizes have been determined by X-rays, and the points are for both National Carbon rods and Thermax carbon black powders. The crystallite sizes were changed by heat treating the rods and carbon blacks in steps of 200° from 1200°C to 2800°C. This curve is similar to one of susceptibility vs. HT given by Pinnick in Fig. 15 of his review¹; the region of steepest ascent corresponds to heat treatments from 1600°C to 2200°C.

For very small crystallites of 50 Å diameter or smaller, the observed values of the susceptibility agree well with values estimated for aromatic ring systems (large aromatic molecules) by extrapolation of the anisotropic component to such large diameters and by adding to it the small atomic diamagnetism of the individual carbon atoms⁵. The sharp rise in the susceptibility as the crystallites grow from 50 to 150 Å occurs over the range of HT where the Fermi level is rapidly rising and the effective number of holes in the valence band is decreasing. It is probable that in this region and for

higher HT , the anisotropic part of the susceptibility can be considered to be mainly that of a two-dimensional free electron gas. The surprising thing is that the susceptibility attains a high value at such small crystallite sizes and remains fairly constant for increasing crystallite size. That is, the plateau in the magnetic susceptibility curve extends

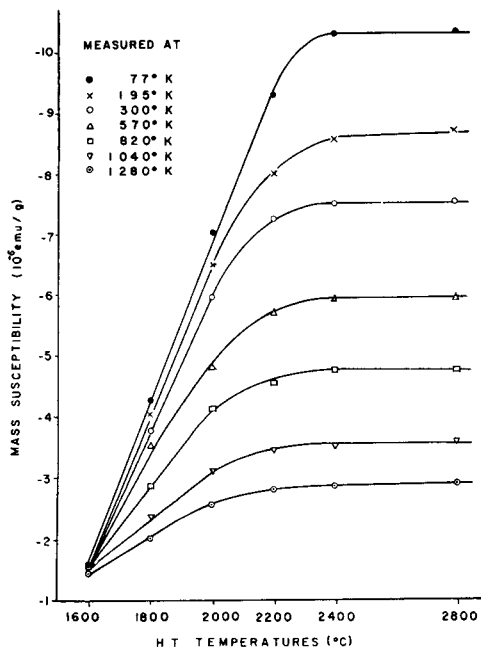


FIG. 4. Magnetic susceptibility vs. heat treatment at different ambient temperatures for National Carbon rods⁴.

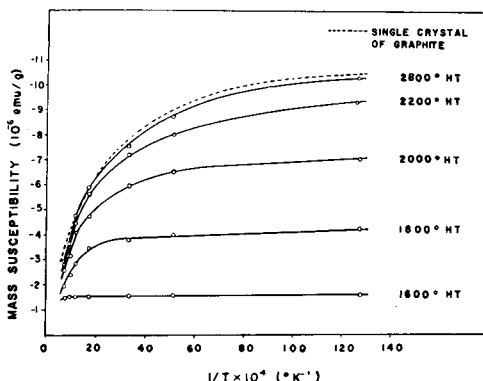


FIG. 5. Magnetic susceptibility vs. $1/T$ for National Carbon rods of different heat treatments⁴.

³ H. T. Pinnick, Phys. Rev. **94**, 319 (1954).

⁴ H. T. Pinnick and P. Kiive, Phys. Rev., April, 1956.

⁵ S. Mrozowski, Phys. Rev. **85**, 609 (1952).

over a region of HT where the Hall effect and thermoelectric effect are changing considerably and where the magnetoresistance shows the greatest variation.

The dependence of the susceptibility of carbon rods on ambient temperature has been investigated and results are shown in Fig. 4 and Fig. 5. In Fig. 4 the susceptibility is plotted as a function of HT for ambient temperatures varying from temperature of liquid nitrogen (77°K) to 1000°C , while in Fig. 5 the susceptibility is plotted against $1/T$ with HT as the parameter. In general, the shapes of all the curves in Fig. 4 are similar. There is a plateau in each curve, but the value of the susceptibility corresponding to the plateau is different for different temperatures, being highest at low temperatures. It can be seen that the beginning of the plateau shifts slightly with ambient temperature, moving towards higher HT for lower ambient temperatures. It seems significant that this shift is of the same order of magnitude as the shift of the peak of the Hall curve and of the minimum of the magnetoresistance.

By introducing bisulfate ions into the carbons it is possible to change the position of the Fermi level without at the same time changing the size of the crystallites and the energy gap. For this reason, residual bisulfate compounds were prepared from samples heat treated in steps of 200° between 1800°C and 2800°C . The susceptibility was determined for several ion concentrations, and the results are shown in Fig. 6. The susceptibility was found to decrease with increased ion concentration. The change in susceptibility is greatest for samples of large crystallite size, that is, samples which were heat treated to very high temperatures.

As of two years ago it seemed that the constancy of the susceptibility with HT in the region of the plateau could be explained by assuming that with increasing HT , as the effective number of holes de-

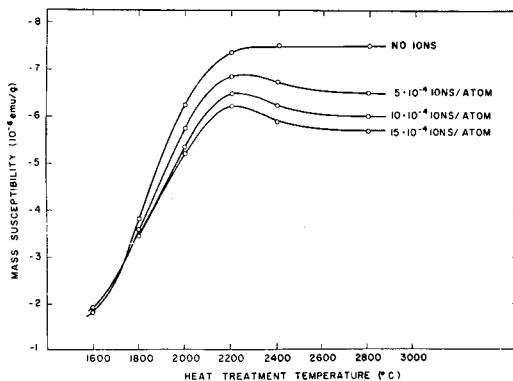


FIG. 6. Magnetic susceptibility vs. heat treatment for carbon bisulfate compounds with three different HSO_4^- ion concentrations⁴.

creased, the curvature of the energy surfaces in the corners of the Brillouin zone changed in such a way as to keep the susceptibility constant.³ But the results for the bisulfate compounds and for the temperature dependence of the susceptibility have shown that the nature of diamagnetism is more complicated than was originally suspected. As of now, there is no theory which explains all the experimental findings.

Another electronic property that has been investigated is the paramagnetic resonance absorption of electrons in carbons. The work has been carried out by J. G. Castle with the help of D. Wobschall. The resonance absorption observed is due to the spin reversal of free or almost free electronic spins. In such an experiment the sample is placed inside a section of a waveguide which is located in the magnetic field, and microwave radiation of a fixed frequency is sent through the waveguide. When the magnetic field has just the value for which the Larmor precession frequency of the spinning electrons is equal to the microwave frequency, resonance occurs. The sample then absorbs energy, and this absorption is detected by the apparatus. Fig. 7 is a schematic diagram of the apparatus used.

These experiments yield three kinds of

MAGNETIC RESONANCE SPECTROMETER

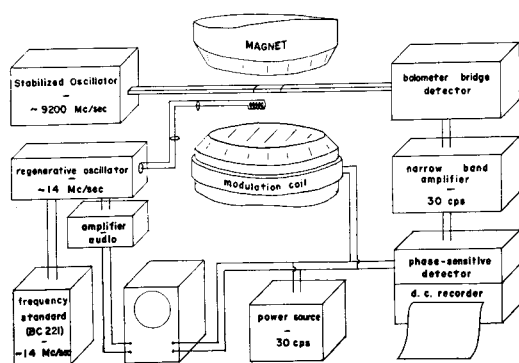


FIG. 7. Block diagram of paramagnetic resonance absorption apparatus.

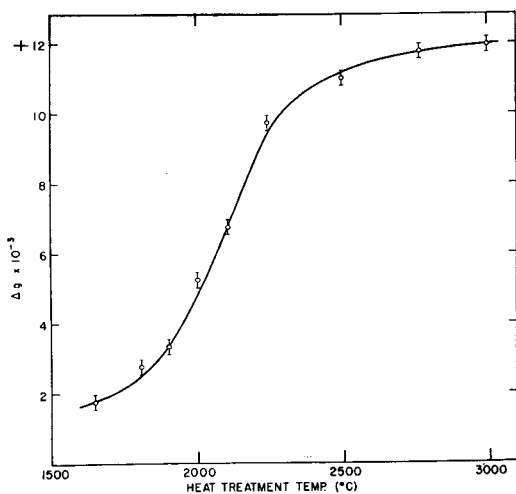


FIG. 8. Difference between observed g -value and spin-only g -value as a function of heat treatment for Thermax carbon blacks⁷.

information: g values, relaxation times, and relative intensities. By comparing the observed g value (spectroscopic splitting factor) with that for a free electron, one gets an idea of how "free" the spin moment of an electron in the solid actually is. The g values observed in carbons are all close to but slightly greater than the spin-only (free spin) value. The g value observed in soft carbon powders⁶ in the range of heat treatments from 1600 to 3000°C is equal

to 2.005 and is constant to within a fraction of the line width over the whole range of heat treatments. This is the same g value that has been previously published for graphite (See ref. 12 in Pinnick¹). The relaxation times are inversely proportional to the width of the absorption lines. The absorption lines for the soft carbons are asymmetric in shape, and the line widths, as determined by the separation between the minima and maxima of the derivative signal, show a variation with HT in the region between 1600°C and 3000°C. There is an almost continuous variation of line width with HT , with maxima at 1600°C and 2400°C and a minimum near 2100°C.⁶

In carbon blacks, narrower absorption lines are observed, as well as an interesting variation in the g value with HT .⁷ The blacks have been investigated both for their own sake and in the hope that the results would also shed some light on the behavior of soft carbons. Fig. 8 shows Δg , the difference between the observed g value and the spin-only g value (2.0023) for Thermax carbon blacks that have been heat treated from 1500°C to 3000°C. The g value is observed to be very close to the spin-only value at 1500°C and then to increase fairly rapidly with increasing HT . The half widths of the absorption lines, which are proportional to the relaxation rate, are fairly constant for most of the range, but increase at both low and high heat treatments. From a HT of about 1600°C toward lower heat treatments the intensity of the signal rapidly decreases. The width of the absorption line increases so that the effect observed is probably that of a line so broad that no signal can be detected. In fact, for carbons heat treated between 1400°C and 700°C, no signal was observed.

However, for raw cokes in the HT range from 300°C to 700°C an absorption line is again observed.⁸ Raw cokes obtained from

⁷ J. G. Castle, Jr., Phys. Rev. **99**, 341 (1955).

⁸ J. G. Castle, Jr., Phys. Rev. **98**, 1564 (1955).

⁶ J. G. Castle, Jr., Phys. Rev. **95**, 846 (1954).

cellulose, styrene, coal, polyethelene and other sources were found to have a constant g value of 2003, a little greater than the spin-only value, over the entire range of HT from 300°C to 700°C. The half widths of the absorption lines varied from sample to sample, but it appeared that the soft cokes had slightly larger half widths (shorter relaxation times) than the hard cokes. Also, the intensities of the absorption lines increased from a heat treatment of 300°C to a maximum between 400°C and 600°C, and then decreased rapidly toward 700°C as increased amounts of volatile material were driven out of the coke. The intensity depends on the atmosphere surrounding the sample during heat treatment as well as on the heat treatment temperature. The experiments indicate that the spin absorption probably takes place in peripheral groups attached to the raw coke molecules which in some cases might be derived from the nitrogen or oxygen in the furnace atmosphere during heat treatment.

It was also found that the oxidation produced by grinding graphite in air caused a very large increase in the intensity of the absorption signal observed in paramagnetic resonance. However, when the graphite powder was subsequently heat treated in a nitrogen atmosphere to a temperature of 1000°C, the effect due to the grinding was removed as the intensity of the absorption signal decreased to its value before grinding. The paramagnetic resonance experiments offer a great amount of interesting information, but the relations between different experimental results appear at the present time to be rather complicated. Paramagnetic resonance absorption in carbons, along with the negative magnetoresistance and the magnetic susceptibility, constitute three major unsolved problems concerning the electronic properties of carbons.

Another electronic property which was under investigation is the infrared absorption and spectral response of raw coke films.

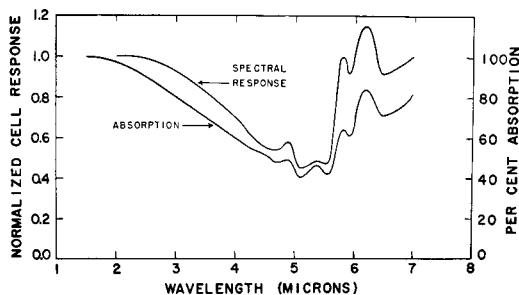


FIG. 9. Absorption and spectral response of a raw coke film in the infrared. The film was a thin sheet of cellophane heat treated in a nitrogen atmosphere to 600°C⁹.

This work has been done by J. F. Andrew.⁹ The raw coke films were mainly thin sheets of cellophane or polyacrylonitrile films that were heat treated in a nitrogen atmosphere between 300°C and 700°C. An infrared spectrometer was used to obtain monochromatic radiation. The raw coke films absorb radiation and their resistance decreases when they are illuminated. The change in the resistance of the film while under illumination is called the spectral response.

In Fig. 9 both the absorption and response are plotted as a function of wavelength for a raw coke film prepared by heat treating a thin sheet of cellophane to a temperature of 600°C. It can be seen that the curves are very similar in shape. Previous work had shown that the absorption edge, or drop in the absorption at the short wavelength end of the curve near 2 microns, shifts with HT . As the temperature of HT increases, the absorption edge shifts to longer wavelengths, corresponding to a decreasing energy gap with increased HT .¹ The main process occurring in this low wavelength region is the photo-excitation of electrons from the valence band to the conduction band. The energy released by the recombination of the hole-electron pairs created by this photo-excitation causes heat-

⁹ J. F. Andrew, J. Opt. Soc. Am. **46**, 209 (1956).

ing of the film. This process is effective only for quanta whose energies are equal to or greater than the gap energy. For quanta of longer wavelengths, the absorption occurs through molecular vibrations. For these longer wavelengths, the response, or change in the resistance of the film when it is illuminated, is due to the heat directly produced by the absorbed radiation. Consideration of Fig. 9 seems to show that in both regions the response is due to heating of the film. As an additional check, various liquid backings were used for the raw coke films and the response was determined in the

short wavelength or electronic absorption region where photo-excitation occurs. Each liquid caused the spectral response to decrease, but to varying degrees. The degree to which the response decreased depended on the thermal conductivity of the liquid and the degree to which the liquid penetrated the pores of the film. Those liquids which best conducted heat away from the film decreased the response the most. One concludes, therefore, that these raw coke films act in the infrared as thermistor bolometers and not as photoconductors, even in the region where photo-excitation occurs.