

## A Study of ESR of Chars and of Carbon with A-Centers\*

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Since the original discovery of ESR in chars a great number of papers appeared reporting observations on chars made from various organic materials. Unfortunately, lack of precision and care in preparation of the chars and in subsequent measurements has led to a great number of discrepancies in the results and consequently in their interpretation. In particular, frequently the heat treatments were performed under conditions permitting the decomposition gases reacting back with the char and thus creating additional spin centers of an A-type (A for Antonowicz<sup>1</sup>) different from those formed in the char as a result of heat treatment. Furthermore the presence of adsorbed gases on the samples and of microwave saturation have strongly affected the results of the temperature dependence and led some investigators to erroneous conclusions. We have therefore taken two well-defined materials, sugar and polyvinylidene chloride and performed on them careful intensity and temperature studies as a function of heat treatment. For sugar the well-known results are confirmed (intensity maximum  $3 \times 10^{20}$  spins/gram at HTT 700°) but for polyvinylidene chloride (PVC) only a single intensity maximum of  $10^{20}$  spins/gram was found at 500°C HTT with the line broadening and disappearing above 650° HTT, and no resonance reappearing above that (checked up to 1600°C). The temperature dependence is for PVC exactly following the Curie law (observed range 300 - 650° HTT) as well as for the sugar chars (checked for HTT 400°C up), however with a deviation gradually showing up above HTT of 700°C. The ratio  $R = I_{LN}/I_{RT}$  decreases from the Curie value of 3.75 at 700°C down to 2.85 at HTT 900°C (above which the ESR in sugar disappears). It is believed that this deviation is due to mixing of the resonance line of localized centers with the resonance line of conduction carriers appearing at these heat treatments, since the I vs T curve can be split into a sum of Curie and temperature independent component<sup>2</sup> (on plot  $1/x$  vs T roughly a straight line with a Curie-Weiss constant  $\theta < 0$  is obtained).

A-centers were made by oxidation under pressure on sugar heat treated from 800° to 1600° and PVC from 700 to 1600°, as well as on P33 carbon black heat treated from 1000 to 1600°C. It was found that while putting A-centers on the surface of such carbons is relatively easy for some of these heat treatments, in some narrow ranges of heat treatment this becomes very difficult. A-centers on sugar and on PVC exhibit exactly Curie type behavior up to HTT 900°C - the increase in R for sugar char of HTT 800° and 900° after putting on A-centers to Curie value showing the increased contribution of localized spin centers. For chars heat treated to 1100° - 1600°C the ratio R rapidly decreases to values in the range 2.3 - 2.0. A-centers on P33 carbon black give R around 2.2 - 1.8. Samples of P33 with various concentrations of A-centers were prepared in order to study the mixing effect between the ESR of localized A-centers

and the conduction carriers (which evidently possess a very wide ESR line at these heat treatments by themselves, but condense into the narrow line of the A-centers via the mixing effect, and thus lead to the observed deviation from Curie dependence). It was found that the degree of deviation from Curie law does not depend on the concentration of A-centers, thus showing that the mixing effect does not extend over all conduction carriers present in the sample but only over carriers present in surrounding regions limited by diffusion path length. Some comparative studies of the width of lines were carried out on 9.2 and 35 Gc microwave spectrometers for all these materials and these results will also be reported.

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1. K. Antonowicz, Proc. 5th Carbon Conf. 1, 46 (1962)
2. S. Mrozowski, Carbon 3, 305 (1965)