JOURNAL OF APPLIED POLYMER SCIENCE VOL. VI, ISSUE NO. 19, PAGES 94-97 (1962)

Temperature Dependence of Nuclear Magnetic Resonance Absorption in Coal

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The measurements of wide-line proton magnetic resonance provide some insight into the hydrogen distribution and molecular motion in coals. The second moment of the proton magnetic resonance line for coals has been measured at 90 and 77.2°K. by Newman, Pratt, and Richards,[1] and by Smidt, van Raayen, and van Krevelen,[2] respectively. Bell, Richards, and Yorke[3] and Given[4] have estimated the hydrogen distribution in coals. It appears, however, that very few detailed investigations of the temperature dependence of proton magnetic resonance absorption in coal have been made. In this paper we present some results obtained by the wide-line nuclear magnetic resonance (NMR) technique on the vitrain of Yūbari caking coal and its residue of pyridine extraction over the range of 90 to 423°K.

EXPERIMENTAL

The coal specimen was pulverized to pass through a 30 and stand on a 60 Tyler mesh sieve. The vitrain, of specific gravity less than 1.30, was isolated by the float-or-sink method, with the use of a mixture of benzene and carbon tetrachloride. The characteristics of the vitrain of Yūbari caking coal having a homogeneous and polymeric character are shown in Table I.

To exclude the influence of water adsorbed on the vitrain, the specimen was heated to 130°C. under 10^{-3} mm. mercury pressure for 8 hr. and sealed in a glass tube.

The residue of vitrain, extracted with refined pyridine under dried air in a Soxhlet apparatus for 50 hr. (the yield of extract is 27.5% dry, ash-free basis) was dried *in vacuo* at 130°C. for 6 hr. and sealed in a glass tube.

TABLE I
Characteristics of Yūbari Vitrain

Proximate analysis, %			
Moisture	Ash	Volatile matter	Fixed carbon
1.1	2.7	44.9	51.3

Ultimate analysis, % (dry, ash-free basis)				
C	H	O	N	S
84.9	6.2	7.1	1.8	0.0

Fraction of crystalline-phase carbon in the vitrain by x-ray analysis, 0.85 (K. Egi, private communication, unpublished data).

The wide-line NMR spectrometer (balanced tube-type bridge) was used and the method of temperature measurements have been reported elsewhere.[5] Proton resonance measurements of the vitrain and the extraction residue were made over the range of 90 to 423°K.

RESULTS AND DISCUSSION

Figures 1 and 2 show one half of the first derivative of the proton absorption as a function of the applied magnetic field for the vitrain and the extraction residue at various temperatures. The absorption in the vitrain consists of only one broad component at 93 and at 293°K., a broad component with shoulder at 343°K., and a broad and narrow component at 423°K. The absorption in the extraction residue consists of only one broad component at 91 and 293°K., a broad component with shoulder at 363°K., and a broad and narrow component at 423°K.

For these phenomena it may be possible to propose one of the following explanations: (*1*) that

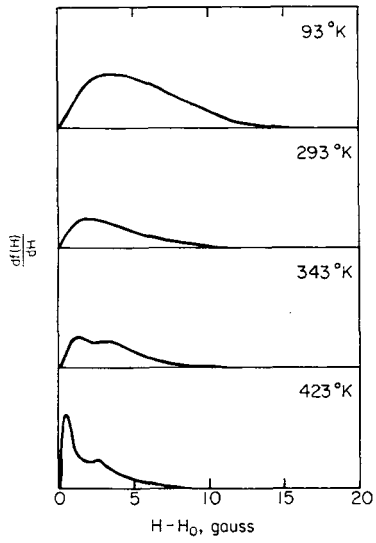

Fig. 1. First derivative of the proton resonance as a function of the applied magnetic field in Yūbari vitrain (one half of the experimental record is shown).

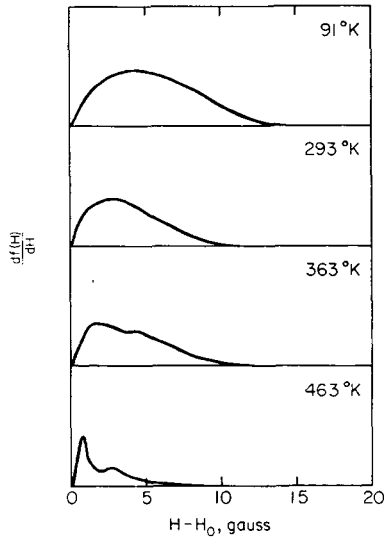

Fig. 2. First derivative of the proton resonance as a function of the applied magnetic field in pyridine extraction residue of Yūbari vitrain (one half of the experimental record is shown).

the contribution of aromatic hydrogen atoms and aliphatic or alicyclic hydrogen atoms present in coal varies with temperature, or (*2*) that the contribution of crystalline portion and amorphous portion present in coal varies with temperature. Moreover, the explanation may be proposed that the contributions of the lower molecular part, such as tarry material or so-called bitumen contained originally in coal, and the remainder of the coal vary with temperature. As the variation of the

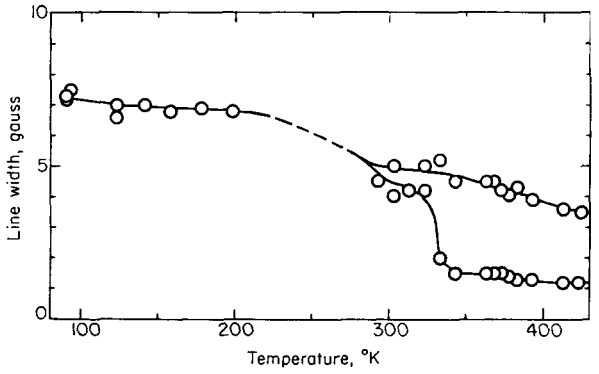

Fig. 3. Variation of the line width with temperature for Yūbari vitrain.

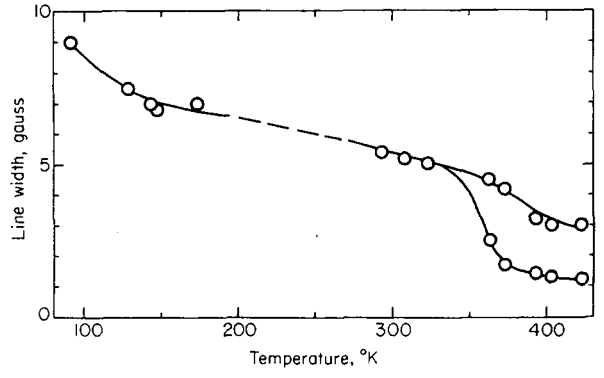

Fig. 4. Variation of line width with temperature for pyridine extraction residue of Yūbari vitrain.

absorption line in the vitrain and the extraction residue with temperature show the same phenomena, however, the last explanation is denied.

X-ray studies of coal have established that the crystalline phase and the amorphous phase coexist in vitrain: namely, the ordered portion and the disordered portion.[6] Several investigators,[7] on the other hand, reporting a consistency in the results of NMR and x-ray studies in polyethylene, have assigned the broad component to the crystalline phase and the narrow component to the amorphous phase, and have attempted a "per cent crystallinity" from the measurements of relative intensities of the two components. Therefore it may be possible to apply this idea to coal, but further precise discussion would be expected from prospective studies.

Figures 3 and 4 show the variation of the line width with temperature for the vitrain and the extraction residue, respectively. The line width was taken as the separation, in gausses, between the corresponding maxima and minima of record of

the first derivative of the absorption with respect to the applied field. In the vitrain the line width of the broad component is constant at a value of about 7 gausses at 90–198°K. Above this latter temperature the line width decreases to a value of about 5 gausses in the vicinity of 300°K. Then the line width of the broad component decreases gradually with temperature and reaches 3.5 gausses at 423°K. At about 300°K. a narrow component resolves from the broad component. The line width of the narrow component decreases rapidly with temperature in the vicinity of 333°K., then decreases gradually with temperature up to 423°K. and reaches 1.2 gausses. The line width variations in the extraction residue are very similar to those observed in the vitrain, but the rapid decrease of the narrow component occurs at a temperature a little higher.

Bloembergen, Purcell, and Pound[8] have shown that NMR line width is sensitive to the amount of molecular motion present in a system; i.e., the more violent the molecular motion, the narrower the line width. Therefore the line width in the vitrain and the extraction residue depends upon the extent and type of molecular motion in them. And the rapid narrowing of the line width of the narrow component in the vitrain and the extraction residue at about 333 and 360°K., respectively, suggests a glass transition attributed to the molecular motion. For Yūbari vitrain, we have already found the glass transition in the neighborhood of these temperatures by a dilatometric method and two different hardness methods.[9] It appears that the results obtained by NMR absorption are not inconsistent with those obtained by the dilatometric and hardness methods. Consequently, it may be supposed that vitrain has a structure like that of a linear polymer.

More information about the type of molecular motion in coal may be obtained from the variation of the second moment of the absorption line with temperature. Figures 5 and 6 show this variation for the vitrain and the extraction residue, respectively.

In the vitrain, the second moment decreases with temperature from 16.0 gausses^2 at 90°K. But the second moment remains approximately constant at about 10 gausses^2 from 293 to 368°K. and then decreases with temperature above 368°K. In the case of the extraction residue, the second moment decreases gradually with temperature from 18.9 gausses^2 at 91°K. However, it can be seen that this decrease occurs in three distinct phases, with only a relatively small decrease occurring between about 300 and about 350°K.

At 423°K. the value of the second moment for the vitrain and the extraction residue is about 7 gausses^2 or so, and higher than those for the general synthetic high polymers. This suggests that coal has a stiffer structure, depending on the hydrogen bonding force, van der Waals force, and so on among the coal base units, than general synthetic high polymers.[9]

As the constitution of coal is complex, it is impossible to calculate the second moment of the absorption line for the vitrain and the extraction residue. Therefore little information on the molecular structure or the type of molecular motion in coal can be gained from a study of the variation of the second moment with temperature. It is clear, however, that some form of molecular motion must be occurring in the vitrain and the extraction residue in the vicinity of 90°K., because the decrease of the second moment in these samples is observed in the neighborhood of 90°K., as shown in Figures 5 and 6.

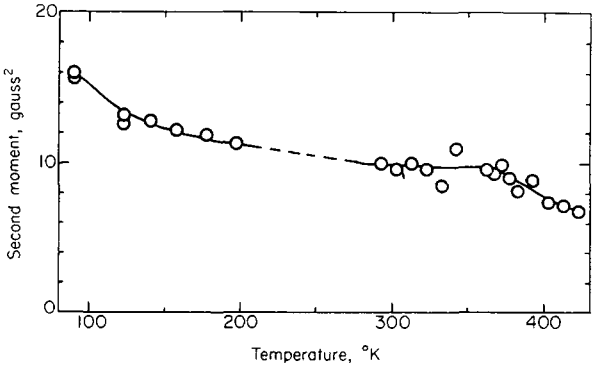

Fig. 5. Variation of second moment of the absorption line with temperature for Yūbari vitrain.

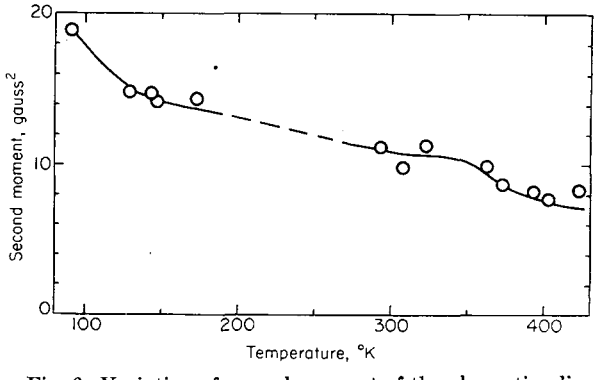

Fig. 6. Variation of second moment of the absorption line with temperature for pyridine extraction residue of Yūbari vitrain.

Bell, Richards, and York[3] attempted to estimate the ratio of aromatic hydrogen atoms to hydrogen atoms in CH_2 groups from the NMR spectra of crystalline hydrocarbons. Their view is based on a general conclusion that the molecules in many hydrocarbons are rigid at 90°K., except the methyl groups, which undergo hindered motion about their C_3 axes. Generally, the motion of methyl groups greatly reduces their contribution to the total second moment. The second moment of the NMR line for three different coals at 90°K. was measured by Newman, Pratt, and Richards.[1] Bell et al.[3] used the Newman results in making a tentative estimation of the ratio of (aromatic + methyl) hydrogen atoms to hydrogen atoms in the CH_2 and perimethyl groups employing the above-mentioned relationship for hydrocarbons. From Figures 5 and 6, however, it is clear that their results must be regarded as very tentative.

On the other hand, a marked difference exists in the values of second moment obtained by Smidt, van Raayen, and van Krevelen[2] at 77.2°K. and those obtained by Newman et al.[1] at 90°K. Smidt et al. believed that this difference is due not to the slight difference in measuring temperatures but to the influence of water absorbed on the coal.

Therefore, it appears that extensive studies of these problems are necessary.

The authors are indebted to Messrs. Y. Koike and T. Uetake for performing much of the experimental work. Thanks are due also to Mr. K. Egi for use of the results of x-ray analysis.

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Synopsis

The proton magnetic resonance in the vitrain of Yūbari caking coal and its residue of pyridine extraction has been studied over the range 90 to 423°K. At lower temperature the absorption line consists of a broad component. At higher temperature this component begins to decrease rapidly in the line width and resolves into two components. This rapid narrowing of the absorption line width suggests a glass transition attributed to the molecular motion in coal. The variation of the second moment of the absorption line with temperature reflects the line width variation. From these results some information on the molecular motion and arrangement in coal have been obtained.

Résumé

La résonance magnétique nucléaire du proton du charbon Yūbari et de son résidu d'extraction à la pyridine a été étudiée dans un domaine de température allant de 90° à 423°K. Aus basses températures, l'absorption est constituée par une large bande. À plus haute température la largeur de la bande diminue rapidement et l'absorption se résoud en deux composantes. Ce rétrécissement rapide de la largeur de la bande d'absorption suggère l'existence d'un point de transition vitreuse dû au mouvement moléculaire dans le charbon. La variation du second moment avec la température reflète la variation de la largeur de la bande d'absorption. Au départ de ces résultats, on a pu obtenir certains renseignements sur les mouvements et l'arrangement des molécules dans le charbon.

Zusammenfassung

Es wurden die protonenmagnetische Resonanz von Yūbari-Backkohle und ihres Rückstandes bei Extraktion mit Pyridin in einem Bereich von 90°K. bis 423°K. untersucht. Bei tieferer Temperatur besteht die Absorptionslinie aus einer breiten Komponente. Bei höherer Temperatur beginnt diese Komponente rasch in der Linienbreite abzunehmen und löst sich in zwei Komponenten auf. Diese rasche Verengung der Absorptionslinienbreite weist auf eine Glasumwandlung hin, die auf die Molekülbewegung in der Kohle zurückzuführen ist. Die Änderung in der Linienbreite spiegelt sich in der Änderung des zweiten Moments der Absorptionslinie mit der Temperatur wider. Aus diesen Ergebnissen wurden einige Informationen über die Molekülbewegung und- anordnung in der Kohle erhalten.

Received August 15, 1960
Revised March 6, 1961