Rheology of Coal. II. Structure of Coal and Its Internal Viscosity at Audiofrequencies*

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(Received July 7, 1952)

Introduction

Previous experiments on Young's moduli of coals by using a resonant frequency method(1) show that the elastic constant used as a measure of bond strength in solids describes the essential properties of coal in absolute units. A theory is proposed that coal is composed of independent molecules possessing similar crystallographic meaning and a more or less highly developed aromatic character, held together by van der Waals' forces of varying strength. These results also show that the experimental Young's moduli can be expressed by the equation,

$$E=E_0(1+K\phi) \qquad (1)$$

where, E=Young's modulus of the coal specimen, E_0=Young's modulus of "pure" coal molecules, ϕ=volume concentration of ash in the specimen, and K=a constant representing the degree of solvation. The values of E_0 and K are constants for each coal species and describe the properties of the coal. With a typical strongly-caking coal, the intermolecular forces would be expected to be small and at the same time the solvation of coal molecules by ash as skeleton should be most strong (see later). Furthermore, the physical meaning of the principal chemical theories for caking properties, i. e., the bitumen theory of F. Fischer et al.(2), or W. A. Bone and others(3) and also the gamma theory of R. V. Wheeler and his collaborators,(4) can be obtained from the Young's modulus measurements and a relationship between ash concentration and bitumen content. About the definition of caking, see Ref. 1.

If Equation 1 is valid, another linear function will exist between the internal viscosity and ϕ, because, theoretically Young's modulus and internal viscosity of solids containing "filler" show the same relationship respectively with filler volume concentration (Ref. 13 and 14). Also it may be possible to relate the phenomena of caking with viscosity measurements. With this in mind the experimental study measuring the internal viscosity at audiofrequencies by a vibration method were carried out.

Experimental

Although several experimental methods for measuring the dynamic properties of rubber-like solids(5) and tyre cord(6) have been described recently, they cannot be used with coal, because specimens of sufficient length are unobtainable and of differences in the rheological properties. Young's moduli of coal specimens can be measured with a crystal pick-up,(1) but this method is not adapted for the internal friction measurements, as the vibrational energy is characteristically dissipated by the Rochelle salt crystal. For the present purpose the author has constructed an apparatus as shown schematically in Fig. 1. The

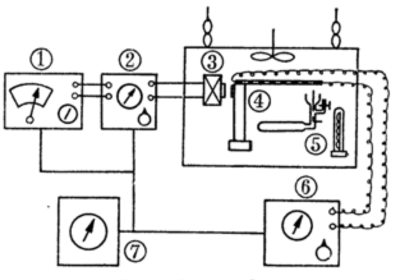

Fig. 1.—Experimental apparatus.
1. Oscillator 2. Amplifier 3. Magnet
4. Sample and Pick-up 5. Thermo-regulator
6. Amplifier 7. Voltage Stabilizer

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* Presented at the Colloid Chemistry Symposium, Nov., 1950.

(1) K. Inouye, *J. Colloid Sci.*, **6**, 190, (1951).

(2) F. Fischer et al., *Brennstoff-Chem.*, **5**, 299, (1924), **6**, 33, (1925).

(3) W. A. Bone et al., *Proc. Roy. Soc.* (*London*), **A 105**, 608, (1924); *Trans. J. Soc. Chem. Ind.*, **44**, 291 T, (1925).

(4) R. V. Wheeler et al., *Trans. J. Soc. Chem. Ind.* **103**, 1704, (1913), **109**, 707, (1916).

(5) S. D. Gehman, D. E. Woodford and R. B. Stambaugh, *Ind. Eng. Chem.* **33**, 1032, (1941); J. H. Dillon, I. B. Prettyman and G. L. Hall, *J. Appl. Phys.*, **15**, 309, (1944); A. W. Nolle, *J. Appl. Phys.*, **19**, 753, (1948); R. S. Witte, B. A. Mrowca and E. Guth. *J. Appl. Phys.*, **20**, 4881, (1949).

(6) W. J. Lyons and I. B. Prettyman, *J. Appl. Phys.*, **18**, 586, (1947).

Table 1

Descriptions of Samples

Sample	Origin	Classification	Caking Property	Volatile Matter, Mean Value (dry, ash-free basis)
American	U. S. A.	Bituminous	Strongly caking	35
Takashima	Kyushu, Japan	Bituminous	Strongly caking	38
Toro	Saghalien, U. S. S. R.	Bituminous	Weakly caking	46
Yubetsu	Hokkaido, Japan	Producer gas coal	Non-caking	64
Shosaku	China	Anthracite	Non-caking	7.7

calibrated audiofrequency oscillator sends alternating current from 50 to 10,000 c./sec. to the coil of an electromagnet through a power amplifier of 3.2 watt. Vibration of specimen with magnet and light iron plate cemented on the specimen opposite to the magnet is detected by "U-effect" of a capillary pick-up, and leads to the voltage amplifier of 55 decibels. The "U-effect" was recently discovered by S. Ueda and coworkers,(7) and is the electric voltage produced by mechanical vibration of a capillary within which are many mercury and electrolyte drops arranged alternately. The capillary pick-up used in these experiments has a length of several cm and diameter of approx. 0.4 mm., weighs about 0.1 g. including the leads and contains approx. 30 drops of mercury and 30 drops of 1N. H_2SO_4. The pick-up is cemented with bakelite cement to the top of the specimen. The specimen under examination is contained in a thermostat, regulated to 0.05°C., the thermostat being suspended by ropes and rubber cords in order to remove floor vibration.

The assembly of the supporter is important and it is found best to bury one end of the specimen in Portland cement clamping it carefully after the cement has solidified. All parts of the apparatus should be carefully shielded, the out-put of the amplifier being kept constant to avoid induction effect. The errors due to the additional mass at the top of the specimen and to the damping by air were considered to be sufficiently small to avoid consideration.

The specimens were shaped from coal blocks to the form of a rectangular bar with an accuracy of 1% in each dimension, using motor grinder and sandpaper or by grinding on a glass plate with carborundum. All specimens were cut parallel to the bedding plane.

The differential equation of the vibration of bar is assumed after K. Sezawa(8) as below,

$$\rho\frac{\partial^2 y}{\partial t^2}+E\kappa^2\frac{\partial^4 y}{\partial x^4}+\eta\kappa^2\frac{\partial^5 y}{\partial t\partial x^4}+\xi\frac{\partial y}{\partial t}=0 \qquad (2),$$

where, ρ = density of the sample, E = Young's modulus, η = coefficient of viscosity, κ = radius of gyration of cross section, and ξ = coefficient of friction by air. Resolving the above equation assuming the clamped-free bar vibration, E and η can be calculated(9) approximately as,

$$E=\frac{4\pi^2\rho n^2 l^4}{\kappa^2 m^4} \qquad (3),\ \text{and}$$

$$\eta=\frac{2\lambda n\rho l^4}{\kappa^2 m^4} \qquad (4),$$

where, n = resonant frequency, l = length of the specimen, m = a factor corresponding to the mode of vibration, and λ = logarithmic decrement. If the amplitude (out-put voltage of the pick-up) is plotted as a function of the frequency, the familiar resonance curve is obtained. Taking the half value breadth of the curve as Δn, the logarithmic decrement, λ, can be easily calculated according the theory of damping vibration in the first approximation as,

$$\lambda=\frac{\pi}{\sqrt{3}}\frac{\Delta n}{n} \qquad (5).$$

From Equation 4 and 5, η can be calculated from the measurable values of n, Δn, ρ, l and the thickness of specimen. Using small specimens of coal, only the first fundamental mode of vibration can be detected, so "m" is always 1.875.

Results and Discussions

Filler Effect of Ash.—The internal viscosity values were obtained using specimens with various ash contents of five typical coals, as shown in Table 1.

The rectangular bar specimen was at first set in another apparatus for measuring the Young's modulus from the fundamental flexural resonant freqnency,(1) and then, as previously described, buried in the Portland cement, set in the thermostat of 30.0°C. and the resonance curve was measured repeatedly until constant values of n and Δn were obtained. Thus the Young's modulus calculated by Equation 3 from the clamped-free vibration was compared with the value calculated from the flexural vibration method to check the correct mode of vibration, as the flexural vibration method has better accuracy. The results for the Young's modulus are in Reference 1. As

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(7) S. Ueda, F. Tsuji and M. Watanabe, *Bull. Inst. Chem. Research, Kyoto Univ., Japan*, **18**, 108, (1949), **19**, 44, (1949), **20**, 28, (1950).

(8) K. Sezawa, *Rep. Aeronautical Res. Ins. Tokyo Univ., Japan*, No. 45, (1928).

(9) K. Sezawa and K. Kubo, *J. Appl. Phys, Japan*, **1**, 1, (1932); Y. Tani, *J. Appl. Phys. Japan*, **9**, 372, (1940).

described in a later section, the damping properties of coal are markedly influenced by the resonant frequency, so η was measured at about 1400 c./sec. by adjusting the dimensions of the specimen. Some dependence of η on moisture is supposed, but on this point no information was obtained from this apparatus.

The relation between η and ϕ, calculated under the assumption that the density of ash is 2.0, and that of pure coal is 1.2, is shown in Fig. 2.

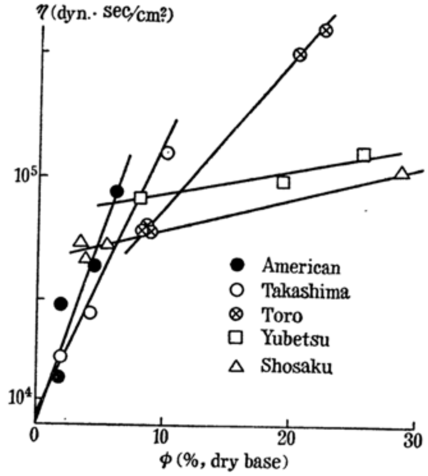

Fig. 2.—Internal viscosity and ash volume percentage.

It is noteworthy, as proposed in the introduction, that η is a linear function of ϕ,

$$\eta=\eta_0(1+K'\phi) \qquad (6),$$

where, η_0 = internal viscosity of pure coal, and K' = a factor representing the solvation of coal molecules with ash. Relation of the same form as Equation 6 has been proved theoretically on dilute suspension by A. Einstein,(10) E. Guth and R. Simha,(11) W. Kuhn(12) and others, and also on solid with filler by E. Guth and O. Gold(13) and E. Guth.(14)

Table 2

Values of η_0 and K'

Sample	η_0 dyn. sec. cm.$^{-2}$	K'	E_0 dyn. cm.$^{-2}$	K
American	1×10^3	16	1.8×10^{10}	38×10^{-2}
Takashima	3×10^3	3.5	2.0×10^{10}	20×10^{-2}
Toro	2.3×10^4	2.7×10^{-1}	3.6×10^{10}	7×10^{-2}
Yubetsu	8.4×10^4	1.0×10^{-2}	4.5×10^{10}	13×10^{-2}
Shosaku	6.8×10^4	1.3×10^{-2}	7.0×10^{10}	-2×10^{-2}

Table 2 describes two constants η_0 and K' characteristic to each coal as well as E_0 and K in Equation 1 from Reference 1. The magnitude of E_0 and η_0 and also of two "solvation factors" K and K' change in the same order, and this fact appears to support the theory and the ash skeleton models of coal structure as illustrated in Reference 1.

The caking properties of coal correspond naturally to the weakness of intermolecular forces as well as strong solvation with inorganic ash portion, namely the molecules of the caking coal become mobile at some elevated temperatures for their weak attraction and thermal stability, by the plasticizer effect of the nonsolvated molecules, in contrast to the non-caking coal molecules which decompose before such plastic condition is accomplished because of their too strong intermolecular forces.

Plasticizer Effect of Bitumen.—The bitumen is the fraction of coal molecules held together with weak van der Waals' forces so as to be extracted by benzene at 300°C. in an autoclave. The points of the chemical theories of caking properties have been that the bitumen is necessary to the caking coal(2) and that its relative relationship to residual parts is important.(3)

The author has shown(1) a relation between ϕ and bitumen content B (in %, dry, ash-free base) applicable to all bituminous coals, i. e.,

$$\phi=\frac{7.5\times10^3}{B^2} \qquad (7).$$

Substituting ϕ of Equation 6 by ϕ of Equation 7, a relation between η and B is obtained. Thus using the values of η_0 and K', η can be calculated for corresponding experimental B values. Table 3 shows calculated viscosity values compared with the measured values.

The bitumen content was determined on the same specimens previously used for measuring the internal viscosity. The specimen was powdered to pass 60 Tyler mesh sieve, dried one hour at 105°C., weighed, and five grams of the sample and 100 cc. of pure benzene were put in an autoclave. The autoclave was shaken automatically throughout the extraction, heated electrically up to 300°C. in 2.5 hours and retained at this temperature for 3 hours. The pressure was about 50 atmospheres. The extracted sample was washed with benzene in a Soxlet apparatus and then dried. The bitumen content was calculated from the difference of ash contents between the original and this extracted sample, assuming that no ash was moved into the bitumen. Fig. 3 shows the relationship between B and experimental η values.

As the relation between Young's modulus and B,(1) these results suggest the physical meaning of chemical bitumen theories, namely on one hand the plasticizer effect of bitumen molecules remarkably reduces the rheological values and on the other hand, perhaps, the importance of relative nature with residue. For instance, Toro (weakly caking) coal has lower bitumen content

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(10) A. Einstein, *Ann. Phys.*, **19**, 289, (1906); **34**, 591, (1911).

(11) E. Guth and R. Simha, *Kolloid-Z.*, **74**, 147, (1936).

(12) W. Kuhn, *Kolloid-Z.*, **62**, 269, (1933); **68**, 2, (1934).

(13) E. Guth and O. Gold, *Phys. Rev.*, **53**, 322, (1938).

(14) E. Guth, *J. Appl. Phys.*, **16**, 20, (1945).

Table 3

Calculated and Experimental Viscosity

Sample	η_0 dyn. sec. cm^{-2}	K'	B, %	η_{calc}	$\eta_{exp.}$
American	1×10^3	17	36.67	9.6×10^4	9.4×10^4
			55.63	4.2×10^4	4.8×10^4
			70.00	2.7×10^4	1.9×10^4
Takashima	3×10^3	3.5	24.30	1.4×10^5	1.1×10^5
			35.72	6.5×10^4	4.5×10^4
			50.53	3.4×10^4	2.7×10^4
Toro	2.3×10^4	2.7×10^{-1}	8.77	6.3×10^5	1.5×10^5
			15.63	2.1×10^5	8.0×10^4
			21.37	1.2×10^5	7.8×10^4
			32.60	6.7×10^4	7.8×10^4

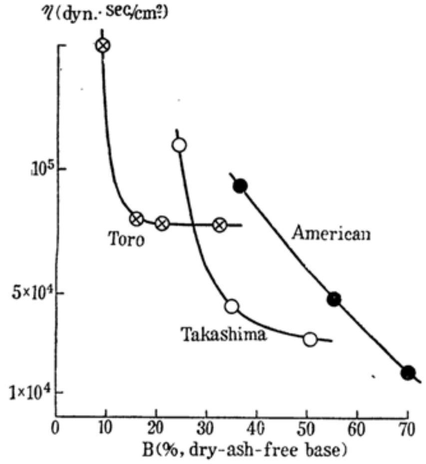

Fig. 3.—Internal viscosity and bitumen content

even in its saturation state, at higher viscosity values, in other words, the bitumen in this coal is less effective as plasticizer, and it is suggested that improvement of the relation between bitumen and residue (or, of some inner condition) is necessary, before the coal is used as better caking coal.

Dependence of Frequency and Temperature.—To elucidate the dependence of internal viscosity on frequency, three typical specimens of American strongly-caking coal, Yubetsu producer gas coal and Shosaku anthracite were selected, the dimensions of which were large enough at first for taking η values of the same specimens at various resonant frequencies by changing the dimensions occasionally. Such measurements were carried out at 30.0, 45.0, 60.0 and 70.0°C. The measurable frequency range was from ca. 400 to 950 c./sec. Detailed values are ommitted from this paper for the limitation of approved space of this Bulletin.*

At each temperature, E and η decrease with increasing frequency. At any given frequency, η of the strongly-caking coal decreases more markedly with increasing temperature, than of the producer gas coal and the anthracite. E does not decidedly change within this range of temperature.

There is at present no theoretical basis, using a relaxation distribution function, to interpret this dispersion. However, at least qualitatively, the decrease of η of the caking coal even in such low temperature range seems to be interesting as to characterize its rheological properties. Taking η values of the American coal for four different temperatures at 600 c./sec. on the graphs, an activation energy is about 1 kcal./mol., calculated by the Andrade formula,⁽¹⁵⁾

$$\eta = Ae^{U/RT} \qquad (8),$$

where, U=Activation energy of viscosity, T=Absolute temperature, R=Gas constant, and $A=a$ constant. It may be interesting to note that the activation energy of viscosity is slightly lower than the energy of thermal motion, RT, at caking temperature, say ca. 1.4 Kcal./mol. at 450°C., provided the activation energy is constant up to such high temperatures.

Although the author has to state that much theoretical and experimental work should be carried out before further detailed discussions can be done, he suggests that the caking properties are due chiefly to the remarkable decrease of friction in the viscosity element, with low activation energy, instead of thermal stability of *intra*-micellar conditions, i. e., the whole system, when the temperature is elevated, fuses and swells by low viscosity of bitumen (or, more freely combined) molecules as plasticizer when the micells, in which the molecules are more strongly combined by the solvation forces with ash portion, exist presumably unchanged. This condition is expected to be accomplished more easily than when all molecules in the system have to become mobile.

The author acknowledges with sincere thanks the enthusiastic assistance of Hideo Tani, and

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* The results are given in the Reports of the Fuel Research Institute, No. 66, Nov., 1952

(15) E. N. Andrade, *Nature*, **125**, 580, (1930).

Mitsuo Abiko during the investigation. He is also indebted to Dr. T. Shimmura, Dr. M. Kurokawa and Mr. A. Baba (this Institute) for their interest in this work. Thanks are expressed to Dr. H. Marsh (King's College, Univ. of Durham) for revising the manuscript.

Shigen-Gijyutsu-Shikenjo (Resources Research Institute) Saitama-Kawaguchi, Japan