# Some Rheological Measurements on Coal Tar Pitches[1]

By Tsurutaro NAKAGAWA

(Received May 2, 1951)

Rheological properties of coal tar pitches in the softening range (80°∼110°) were studied from the following three points of view. (1) They are used as a binding material for the production of some carbonaceous matter, *e. g.*, carbon brush etc., and their practical quality is said to be partly related to the rheological properties of the binder. (2) Highly viscous substances usually behave as visco-elastic, *i. e.*, they have some elastic nature besides being viscous. Rheological anomalies of these substances may be ascribed to the visco-elastic effects. (3) Internal structure of some bituminous solid, *e. g.*, pitches, asphalts and coals, makes an interesting problem in the present stage of chemistry of coal. Analysis of rheological data may disclose some one of these points.

## Experimental

As the experimental procedure for studying and analysing rheological behavior of tar pitches, the author took the method of measuring the visco-elastic properties of the material, using a newly constructed dynamic apparatus suitable for the study in the range of seconds∼minutes of period, which should give information about the dynamic modulus and dynamic viscosity much different from those in the audiofrequency range, where much more work has been done.

**Dynamic Method for Measuring Visco-elastic Properties. Method by the Phase Difference.**[2]— Consider a modification of a rotation viscometer (Fig. 1), and apply the sinusoidal torsional displacement,

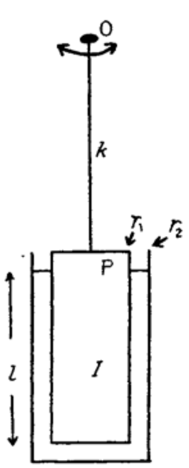

Fig. 1.

$$\Theta = \Theta_0 \sin \omega t ,$$

at the top O of the torsion wire whose torsion constant is $k$ dyne cm., so that the equation of motion of the inner cylinder P is

$$I\ddot{\theta}+R\dot{\theta}+E\theta=k(\Theta-\theta) \qquad (1)$$

where $I\ddot{\theta}$ is the inertial resistance, and $R\dot{\theta}$ and $E\theta$ are the viscous and elastic resistance respectively of the visco-elastic body existing among the two cylinders, and $k(\Theta-\theta)$ is the external torque imposed on the inner cylinder. T. Kuyama[3] suggested a method for studying

---

[1] Read before the 4 th annual meeting of the Chemical Society of Japan on Apr. 8, 1951.

[2] Details of the method will appear in *J. Chem. Soc. Japan*, **72**, 759 (1951).

[3] T. Kuyama, *Kagaku* (*Science*), **16**, 149 (1946).

the visco-elastic effect from the graphical analysis of the stress-strain hysteresis loop.

The author, in the present study, has used a modified scheme. (1) is rewritten as

$$\ddot{\theta}+2\varepsilon\dot{\theta}+n_e^2\theta=L\sin\omega t \qquad (1')$$

$$2\varepsilon\equiv R/I,\ n_e^2\equiv(k+E)/I,\ L\equiv k\Theta_0/I \qquad (1'\text{a})$$

The stationary solution of (1′) is

$$\theta=A\sin(\omega t-\phi)\equiv m\Theta_0\sin(\omega t-\phi) \qquad (2)$$

where $$\tan\phi=2\varepsilon\omega/(n_e^2-\omega^2), \qquad (2\text{a})$$

and

$$m\equiv A/\Theta_0=\frac{k}{I\sqrt{(n_e^2-\omega^2)^2+4\varepsilon^2\omega^2}} \qquad (2\text{b})$$

As is plain from (2a) and (2b), it is possible to calculate $R$ and $E$ from the observed phase difference $\phi$ and the amplitude ratio $m$ at the stationary state of the forced oscillation, by using the next relations

$$\left.\begin{aligned} R&=\frac{kT\sin\phi}{2\pi m}\\ E&=k\left(\frac{\cos\phi}{m}-1\right)+\frac{4\pi^2 I}{T^2}\end{aligned}\right\} \qquad (3)$$

where $T$ is the period ($\omega=2\pi\nu=2\pi/T$).

If $R$ and $E$ are determined, viscosity $\eta$ poises and rigidity $G$ dyne/cm.$^2$ of the substance are known from the following formulas⁽⁴⁾⁽⁵⁾:

$$\left.\begin{aligned} \eta&=\frac{R}{4\pi l}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)\equiv K_0R\\ G&=\frac{E}{4\pi l}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)\equiv K_0E\end{aligned}\right\} \qquad (4)$$

where $l$, $r_1$, and $r_2$ are the lateral length of the immersed portion of the inner cylinder, radius of the inner and the outer cylinder respectively.

In the present measurement the experimental condition is as follows.

$I=8.76\times10^3$ g. cm$^2$.;

$k=1.12\times10^5$ dyne cm. (piano wire of 1 mm. diameter, 72 cm. length);

$r_1=2.50$ cm.; $r_2=3.70$ cm.; $l$, about 16 cm. in all cases;

$\Theta_0=8°45'$ (0.153 radians), so that $A$ is less than that;

$T$, 3 min. to 20 min.; temp., $80\sim110°\pm0.1°$.

In the case of large $T$ as in the present, the term $4\pi^2I/T^2$ in (3) can be omitted. Temperature control was done by the oil bath thermostat regulated in the ordinary manner. Thermal uniformity in the cylinder was so slowly reached for the large dimensions of the vessel that it was necessary to wait about two hours or more before measurement was begun. The sinusoidal motion was supplied by the mechanism of the crank-shaft principle. Deflections $\Theta$ and $\theta$ were read by the method of lamp-and-scale by means of the two small galvanometer mirrors attached to the upper disk and the lower cylinder. The phase angle $\phi$ is given by

$$\phi=\frac{\tau}{T}\times2\pi \qquad \text{radians}$$

where $\tau$ sec. is the measured time interval between the instant when O passes $\Theta=0$ and the instant when P passes $\theta=0$; $\Theta=0$ and $\theta=0$ corresponding to the middle point of the rotational oscillation. The torsion constant $k$ was determined from the period $T_0$ of the free oscillation with a weight of the known moment of inertia $I_0$ by

$$k=4\pi^2I_0/T_0^2.$$

It should of course be kept in mind that $k$ changes with the length of the wire.

**Coal Tar Pitches.**—Pitches from coal tar of ordinary high temperature carbonization were subjected to test. Their origin and the conventional softening temperature are tabulated below (Table 1).

Table 1

| Abbreviation | | Origin | So-called softening point, °C. |
|---|---|---|---|
| Tar pitch | N | Nisshin Kagaku Co. | 80 |
| | O | Osaka Gas Co. | — |
| | H | Hirohata Iron-Works | 79 |
| | Y | Yahata Iron-Works | 65 |

## Results and Discussions

**Frequency Dependence of $\eta$ and $G$.**—Figs. 2 and 3 show frequency dependence of viscosity $\eta$ and rigidity $G$ at various temperatures. As is read from the figures, no appreciable frequency effect upon $\eta$ was observed. Elastic nature is very slight in this frequency range. $G$ cannot be detected at higher temperatures, and becomes appreciable first at lower temperatures. Rheological property of tar pitch so is simply Newtonian for such comparatively

---

(4) E. Hatschek, "The Viscosity of Liquids," G. Bell and Sons, Ltd., London, 1928.

(5) Th. Schwedoff, *J. de Phys.* [2] **8**, 341 (1889).

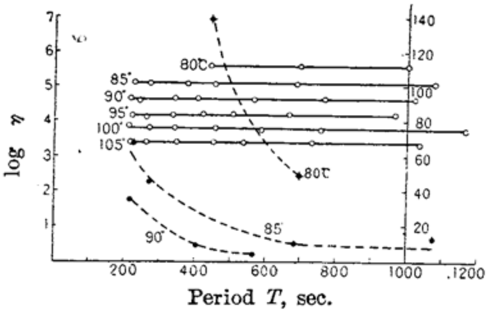

Fig. 2.—Frequency dependence of $\eta$ and $G$ of tar pitch H: —— indicates the frequency dependence of $\eta$ and ----, that of $G$,

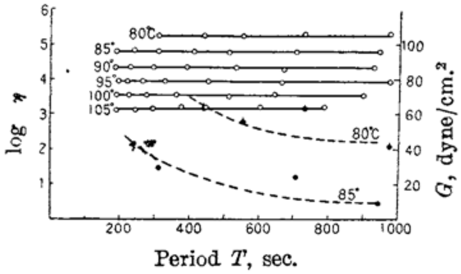

Fig. 3.—Frequency dependence of $\eta$ and $G$ of tar pitch Y: —— indicates the frequency dependence of $\eta$ and ----, that of $G$.

slow observation as in the present case. It is supposed that the time of mechanical relaxation is less or far less than several minutes in these temperatures, so that the mechanisms of elastic strain in the internal structure, if they exist, will decay into the mechanisms of viscous flow in our experimental condition of a long period. Elastic effect may on the other hand become remarkable if they are treated in the range of far larger frequency, *e. g.*, audiofrequency range⁽⁶⁾ for which our experimental device is not available.

From the rheological point of view, frequency dependence of the visco-elastic properties as has appeared in Figs. 2 and 3 will be interpreted as follows. Our whole experimental procedure and scheme of analysing the observed values depend on the assumption that the rheological properties of the material can be simply symbolized by the Voigt model (viscosity and elasticity in parallel) as is schematized in Fig. 4 b. If the material is truly of Voigt type in the rheological behavior, $R$ and $E$, or $\eta$ and $G$ will appear as constant. But, on the other hand, if it is intrinsically of Maxwell type as in Fig. 4 a, the Voigt scheme analysis

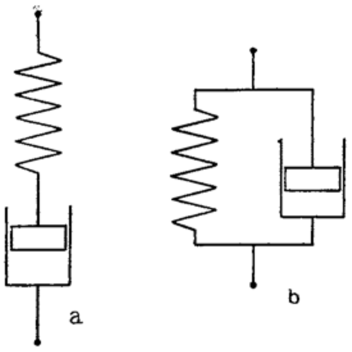

Fig. 4.

of it should lead to $\eta$ and $G$ variant with frequency or amplitude. Assume, now, that tar pitch is a simple Maxwellian body as the first approximation, then the Voigt type analysis of its rheological behavior should bring about the result that viscosity remains constant regardless of period, and that elasticity vanishes with the increase of period. This situation coincides with our observed data.

From the above-stated, it will be admitted that tar pithch is a Maxwellian body (viscosity and elasticity in series, *cf.* Fig. 4 a) with respect to the rheological behavior.

**Temperature Dependence of Viscosity.**— As has been stated above, viscosity is constant in our frequency range. An arithmetical mean of viscosity data at the same temperature was taken as viscosity at the temperature, and was plotted against $1/T$ °K. in Fig. 5. $\eta$ falls to about 1/3 by the increase of 5° of temperature, the sensitivity of $\eta$ to temperature being remarkable compared with the ordinary low molecular weight liquids.

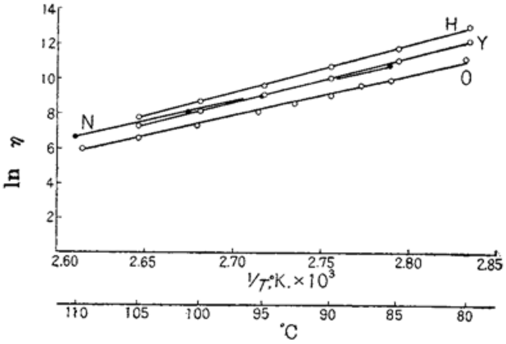

Fig. 5.—Temperature dependence of $\eta$: $\eta = Ae^{B/T}$.

The author has used the Andrade formula

$$\eta = Ae^{B/T} \qquad (5)$$

---

(6) See, for example, J. D. Ferry *et al.*, *J. App Phys.*, **20**, 144 (1949).

to express the temperature sensitivity of $\eta$, and determined $A$ and $B$ by the method of least squares. Results are given in Table 2, and the values for some other materials calculated from other authors' data are shown in Table 3(7) for the sake of comparison. A high value of $B$ indicates that the substance is highly associated, a large amount of energy being necessary to bring about the dissociation. To what is the large negative value of $\log A$ attributed?

Table 2

| Material | $-\log A$ | $B\times 10^{-3}$ |
|---|---|---|
| Pitch N | 23.4 | 23.2 |
| O | 23.7 | 23.2 |
| H | 27.9 | 27.2 |
| Y | 25.5 | 25.1 |

Table 3(7)

| Material | Temperature range, °C. | $-\log A$ | $B\times 10^{-3}$ |
|---|---|---|---|
| Glass below $T_g$(1) | 400∼500 | 23.2 | 63.2 |
| Glass below $T_g$(2) | 400∼500 | 26.0 | 65.7 |
| Glass above $T_f$ | 700∼1400 | 5.6 | 28.6 |
| Undercooled glucose | 22∼40 | 62.4 | 51.8 |
| Undercooled glucose | 110∼145 | 11.7 | 11.9 |
| Rosin | 25∼60 | 44.1 | 38.1 |
| Abietic acid | 20∼50 | 42.9 | 37 |
| Pitch | 20∼40 | 35.6 | 30.9 |
| Asphalt A | 15∼50 | 22.3 | 20 |
| Asphalt A | 80∼130 | 10.8 | 11 |
| Asphalt D | 15∼50 | 22.6 | 20 |
| Asphalt D | 80∼130 | 11.0 | 11 |
| Mercury | −20∼300 | 2.23 | 0.29 |
| Toluene | 0∼100 | 3.76 | 1.04 |
| Water | 0∼20 | 5.44 | 2.32 |
| Water | 50∼100 | 4.36 | 1.56 |

According to the theory of flow by the method of transition state,(8) viscosity $\eta$ is formulated as

$$\eta=\frac{h}{\lambda_1\lambda_2\lambda_3}\,e^{\Delta F^{\ddagger}/RT} \tag{6}$$

where $h$ is Planck's constant, $\lambda$ are dimensions of the unit of flow, and $\Delta F^{\ddagger}$ is the free energy of activation which is necessary for the unit of flow to be activated up to the transition state from its initial state. Further, since $\Delta F^{\ddagger}$ may be replaced by

$$\Delta F^{\ddagger}=\Delta H^{\ddagger}-T\Delta S^{\ddagger},$$

where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ mean the heat of activation and the entropy of activation respectively, it is seen that

$$\eta=\left(\frac{h}{\lambda_1\lambda_2\lambda_3}\,e^{-\Delta S^{\ddagger}/R}\right)e^{\Delta H^{\ddagger}/RT}. \tag{7}$$

From the comparison of (7) with (5) it comes that

$$A=\frac{h}{\lambda_1\lambda_2\lambda_3}\,e^{-\Delta S^{\ddagger}/R},\quad B=\Delta H^{\ddagger}/R. \tag{8}$$

It is therefore, from (8) and Table 2, that

$$\Delta H^{\ddagger}\doteqdot 50\ \text{kcal}.$$

From the rate-process view-point, the high value of $\Delta H^{\ddagger}$ is to be attributed to the fact that, in addition to the normal work required to make a hole, it is necessary for the secondary bonds, whereby a pitch particle is attached to the surrounding particles, to be broken before the activated state for flow can be attained. There is consequently what might be termed as a "structure activation energy", in addition to the normal activation energy, for the flow of such associated fluids as pitch.

The estimation of $\Delta S^{\ddagger}$, on the other hand, will meet with some complexity for the sake of the co-existing volume factor $\lambda_1\lambda_2\lambda_3$. The large negative value of $\log A$ in Table 2 nevertheless postulates that $\Delta S^{\ddagger}$ has a large positive value, which is about 85 E.U. if $\lambda$ is assumed to be 100 Å., while the entropy of activation $\Delta S^{\ddagger}$ is usually negative in the case of flow of the ordinary non-associated substances. If, as suggested above, the unit of flow even in associated fluids is a single particle and the formation of the activated state involves the breaking of a number of secondary bonds, it is evident that the entropy of the activated state will be appreciably greater than that of the initial state. In other words, the entropy of activation for flow $\Delta S^{\ddagger}$ should be relatively large and positive in agreement with our experimental fact.(9)

At the higher temperature, there is no secondary bond that has to be broken before flow

---

(7) The data for constructing this table are borrowed from the following authors. Glass: F. B. Hodgdon and D. A. Stuart, *J. Appl. Phys.*, **21**, 1160 (1950). Glucose: G. S. Parks *et al.*, *Physics*, **5**, 193 (1934). Rosin, abietic acid, and pitch: E. C. Bingham and R. A. Stephens, *Physics*, **5**, 217 (1934). Asphalts: C. U. Pittman and R. N. Traxler, *Physics*, **5**, 221 (1934). Mercury, toluene, and water: "Smithsonian Physical Tables."

(8) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, 1941.

(9) Another example that the high value of $\Delta H^{\ddagger}$ is compensated by the large positive value of $\Delta S^{\ddagger}$ is illustrated in the kinetics of the protein denaturation (cf. note (8)).

can occur, and hence the activation energy $\Delta H^{\ddagger}$ will decrease and the entropy term log $A$ will take a smaller negative value. See the case of glass in Table 3, where $T_g$ is an abbreviation of the German "Temperatur des Glaszustandes" and $T_f$ means "Temperatur des Fadenziehens."

The above-stated conception of the internal structure of tar pitch derived from the analysis of its viscosity in the softening range seems to be reconciled with the theory of the internal structure of coal, in which such nuclei as ash or graphite are considered to be strongly solvated with bitumen. It is probable that in the solid tar pitch, as in coal, the so-called "free carbon" or graphite-like particles are solvated with the bituminous substance, and that such associated structure is conserved even at the softening temperature.

## Summary

(1) Visco-elastic properties of tar pitches in the softening range were measured by a dynamic method covering 3∼20 minutes of period.

(2) No frequency dependence of viscosity was observed in this range of period.

(3) Elastic effect was slight in this range of period. Its frequency dependence was appreciable.

(4) Tar pitch is a simple Maxwellian body rheologically above the softening point.

(5) Temperature dependence of viscosity was studied along the rate-process theory, and it was supposed that tar pitch has a highly associated or solvated structure, consistent with the present theory of the internal structure of coal.

The author wishes to express his gratitude to Professor J. Sameshima and Dr. H. Akamatu for their encouragement. He is also indebted to several organizations (Table 1), for samples. These experiments were largely supported by the Scientific Reseerch Encouragement Grant defrayed from the Ministry of Education, to which the author's thanks are due.

*Department of Chemistry, Faculty of Science,*
*the University of Tokyo, Tokyo*