Viscosity and thermal conductivity of black liquor

Pritham Ramamurthy, Adriaan R.P. van Heiningen, and George J. Kubes

ABSTRACT: Simple techniques were developed to measure the viscosity and thermal conductivity of high-solids black liquor. The method using a Brookfield viscometer for measuring viscosity was modified by applying a thin film of silicone oil on the surface of black liquor to prevent evaporation and skin formation. These two phenomena take place at high temperatures and high solids contents, affecting the viscosity measurements when the conventional method is used. The results of the modified method compared well with the vibrating blade and coaxial cylinders viscometers for a hardwood liquor at 67.7% solids level. A line source method was used to measure the thermal conductivity of black liquor up to 83% solids. We found that the data published earlier by Harvin and Brown (1) could be extrapolated to high-solids contents.

KEYWORDS: Black liquors, solids content, temperature, thermal conductivity, viscometers, viscosity.

The pulp and paper industry is striving to improve the energy efficiency of the kraft mill operation. One way of achieving this is to increase the solids level of the black liquor that is fired into the recovery boiler. The viscosity and thermal conductivity are two physical properties of black liquor that play crucial roles in the operation of a kraft recovery plant. The fluid viscosity determines the power requirements for the pumps, the heat transfer coefficient in the evaporators, and the sprayability and droplet size distribution of the liquor when introduced into the furnace. Thermal conductivity is critical to estimate the rate of heat transfer in the black liquor evaporators and for drying the droplets in the furnace. In this paper, simple techniques are presented for measuring the viscosity and thermal conductivity of black liquor at high solids levels. The thermal conductivity of black liquor has been measured for the first time at high solids levels (53–83%).

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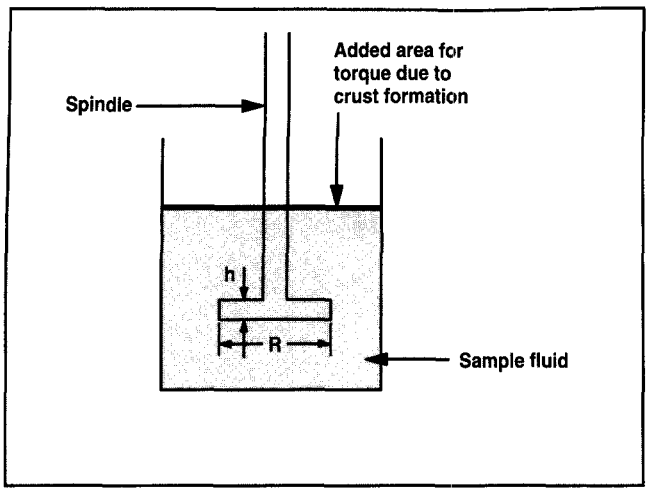
Viscosity of black liquor

In recent years, the measurement of black liquor viscosity has received considerable attention *(2, 3)*. Researchers have carefully studied the influence of temperature and solids content on viscosity using various instruments, most of which can operate under pressure. However, all instruments discussed are prohibitively expensive and fragile for routine mill measurements.

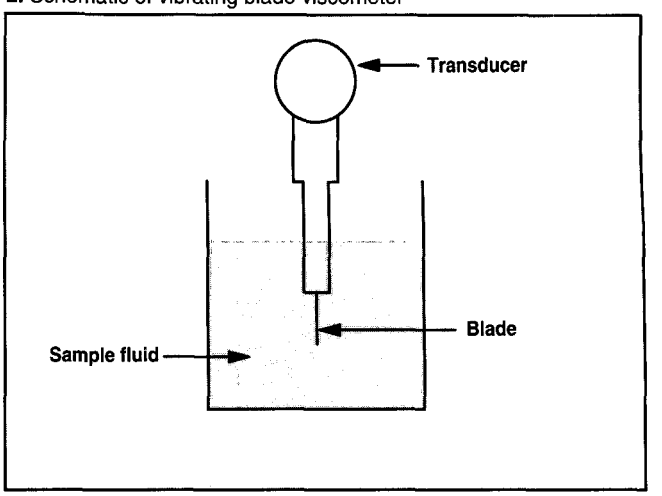
The objective of this study is to present a simple technique for measuring the viscosity of black liquor at high solids contents and temperatures using a common rotating spindle-type viscometer, i.e., the Brookfield viscometer. This is a ubiquitous and rugged instrument. One feature that has prevented acceptance of this viscometer for black liquor viscosity measurements is the exposure of the liquor to an atmosphere that leads to crust formation on the free surface. Since the crust sticks to the spindle, more rotating torque is required, and erroneously high viscosity readings are often obtained.

Boger and Ramamurthy *(4)* studied the influence of evaporation on a Weissenberg rheogoniometer. They prevented evaporation by covering the surface with a very thin film of nonvolatile fluid. This procedure is suggested by the supplier of the Brookfield viscometer *(5)* used in this study, and

1. Schematic of Brookfield viscometer



2. Schematic of vibrating blade viscometer



the same method was adopted here for evaluating black liquor.

Theory

A schematic of the Brookfield viscometer is shown in **Fig. 1.** The torque required to rotate a disc or cylinder in the fluid is measured and converted to viscosity readings, assuming the fluid to be Newtonian. The torque increases with the radius, *R*, and height, *h*, of the disc/cylinder. The torque required to rotate a thin disc in an infinite medium is proportional to the fourth power of the radius *(6)*:

$$Torque \propto \rho R^4 \omega (\nu\omega)^{1/2} \qquad (1)$$

and the torque to rotate a long cylinder in an infinite medium is given by *(6)*:

$$Torque \propto \mu h R^2 \omega \qquad (2)$$

Refer to **Table I** for nomenclature regarding these variables and other variables throughout the paper. The proportionality constants in Eqs. 1 and 2 for a Newtonian fluid, laminar flow, and no end effects can be evaluated exactly as 0.616 π and 4 π, respectively. The shear stress is calculated as:

$$Shear\ stress = Torque\ /\ (area \times arm) \qquad (3)$$

All of the above expressions must be corrected to account for end effects. These effects are accounted for by the viscometer manufacturer, and shear rates achieved at different angular velocities for various spindles are specified in the manuals. The torque is exerted to rotate the spindle according to Eqs. 1 or 2. The shear stress is calculated using the area and arm of the spindle in Eq. 3. The viscosity is calculated as the ratio of shear stress to shear rate and is read from the dial of the viscometer with a suitable scaling factor (depending on the spindle and the shear rate).

I. Nomenclature of variables

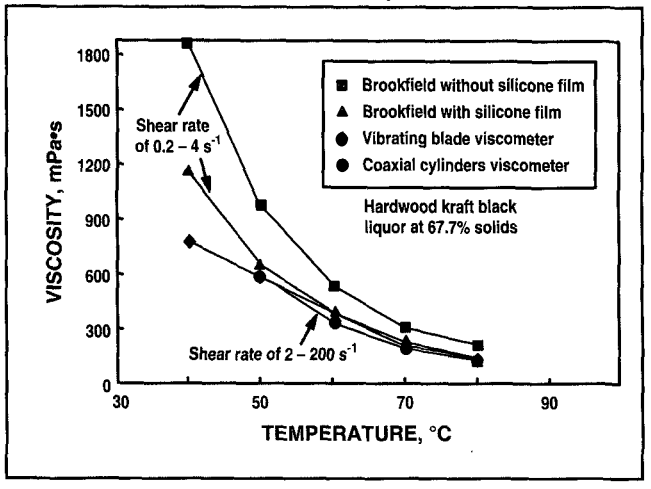
Variable	*Description*
h	Height of cylinder, m
Q	Heat input per unit length, W/m
r	Radius of temperature measurement, m
R	Radius of spindle (disc or cylinder), m
$t, t_0,$	Times for calculating the slope in Eqs. 7 and 8, s
T	Temperature, °C
Z	Exponential integral
α	Thermal diffusivity, m^2/s
γ	Euler's constant, 0.5772156
λ	Thermal conductivity, W/m·K
μ	Absolute viscosity, mPa·s
ρ	Density of fluid, kg/m^3
ν	Kinematic viscosity, μ/ρ
ω	Angular velocity, rad/s

Experimental procedures

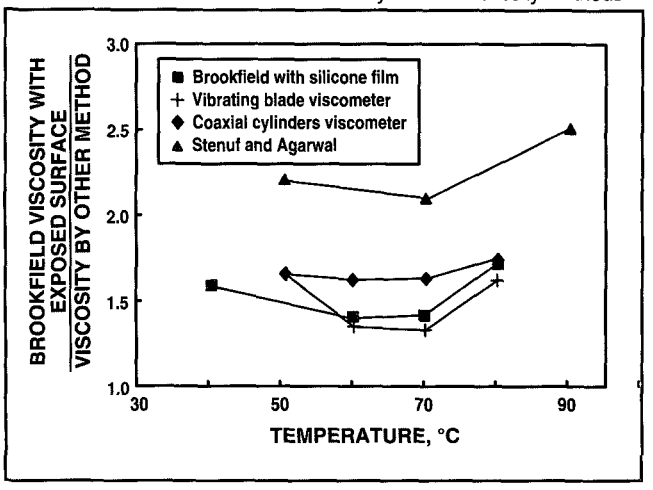
Black liquor was obtained from a local hardwood pulp mill. The solids level of the black liquor was 67.7% as determined by the TAPPI procedure T650 pm-84. The black liquor was homogenized by stirring and was maintained at the desired temperature by a thermostat. The Brookfield viscosities were measured at 20 rpm (shear rates of 2–4 s^{-1}). When a film was used on the black liquor surface, it was a thin film (about 1 mm) of silicone oil. The oil was immiscible with black liquor and had a low specific gravity (about 0.87 g/cm^3 vs. 1.33 g/cm^3 for black liquor). The silicone had a very low viscosity (2.3 mPa·s at 20°C), so its contribution to the drag on the spindle can be neglected.

Two viscometers were used for comparison. One was a Bendix 1800 ultrasonic viscometer. The sensor consisted of a magnetostrictive transducer with a blade vibrating at a frequency of 28 kHz **(Fig. 2)**. When the blade is immersed in a fluid, the vibrations are damped according to the properties of the fluid. The change in pulse frequency

3. Comparison of viscosities measured by different viscometers



4. Ratio of conventional Brookfield viscosity to other viscosity methods



is proportional to the square root of the product of viscosity and density. This product is measured by the viscometer and corrected for the density to obtain the viscosity. The other viscometer used for comparison was a coaxial cylinders unit *(2)*.

Results

Figure 3 shows the influence of the silicone film on the viscosity measurement: the addition of silicone oil reduces the measured viscosity. To verify that the reduction was not due to mixing silicone oil in black liquor, the experiment was repeated with oil films of different thicknesses. Since there was no influence of film thickness on viscosity, the decrease in viscosity was solely due to preventing evaporation at the black liquor free surface.

Figure 3 also shows the viscosity measured with the other viscometers. The data from the coaxial cylinders viscometer were obtained on the same liquor at the University of Florida, Gainesville, by a group led by A. L. Fricke. Note the viscosity readings above 60°C are similar for the vibrating blade viscometer, the coaxial cylinders viscometer, and the Brookfield viscometer with a silicone oil film. Below 50°C, the difference in readings could be due to the non-Newtonian behavior of black liquor, which is pronounced at low temperatures and high solids contents *(2)*.

A crust of approximately the same area is formed with the strong black liquor irrespective of the temperature of viscosity measurement. Hence, the ratio of the measured viscosities with and without crust formation is expected to be independent of the temperature of operation. This is seen in **Fig. 4**, where the ratio of the Brookfield viscosity without silicone film divided by the viscosity measured by other techniques is plotted against temperature. The constant viscosity ratio of about 1.5 implies that the exposed surface introduces an error of about 50% to the measured viscosities.

Also included in Fig. 4 are the data of Stenuf and Agarwal *(7)*, who compared the viscosity measured with a Brookfield unit to that obtained with a flow tube viscometer. The higher ratios obtained by Stenuf and Agarwal could be due to different liquors, surface areas, and shear rates used.

Two precautions are recommended when using the Brookfield viscometer with silicone oil film:

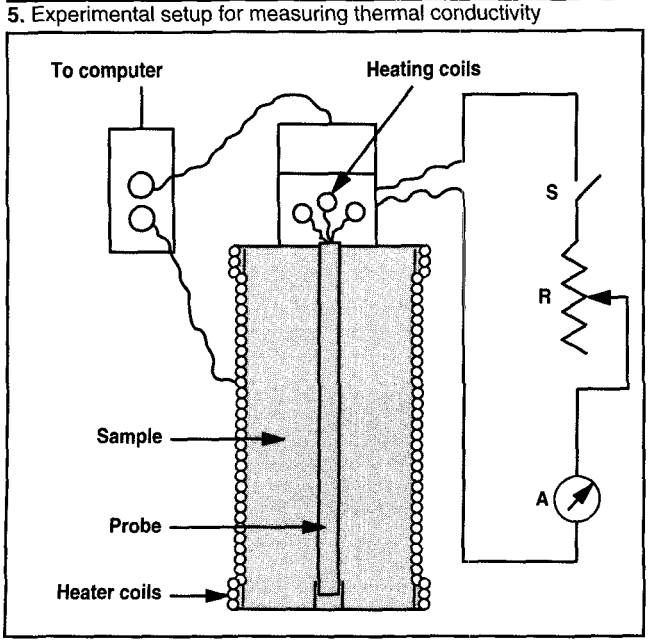
- Ensure that the temperature of the spindle is at equilibrium before recording the viscosity. If the spindle temperature is low, the viscosity of the fluid near the spindle will be relatively high, and erroneous readings will be recorded. Allowing the spindle to turn for about 20 revolutions is sufficient to assure equilibrium. With an exposed surface, this equilibration time is generally sufficient for a crust to form.
- The spindle must be carefully inserted into the black silicone so the liquor oil is not trapped under the spindle disc. This problem can be easily avoided by inserting the spindle into the liquor sample at an angle.

This technique could lead to erroneous results if the fluid exhibits a strong non-Newtonian behavior, which is prevalent for black liquor at high solids contents and low temperatures. Although there is no distinct value, non-Newtonian behavior is generally significant above 70% solids and below 60°C for hardwood liquors.

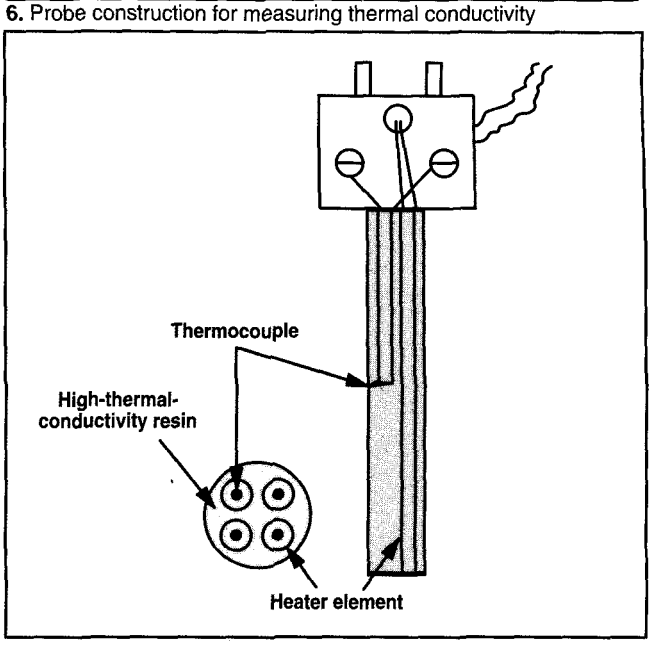
Thermal conductivity of black liquor

Harvin and Brown *(1)* presented an excellent paper on the thermal conductivity of black liquor at solids concentrations to 53%. Since then no additional results have been published, even though the present industrial standard is to fire liquor at a solids level of 66–72%. Because the thermal conductivity of high-solids black liquor could be important in alternative processes such as drum drying or spray drying, this study's objective was to measure the thermal conductivity of black liquor with a simple technique

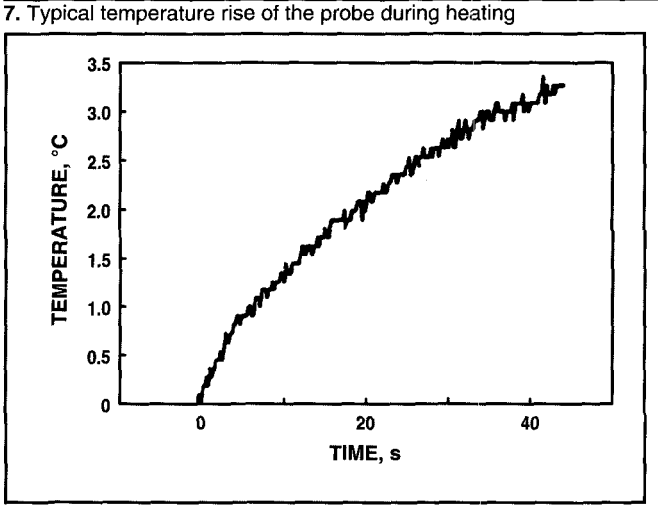
5. Experimental setup for measuring thermal conductivity

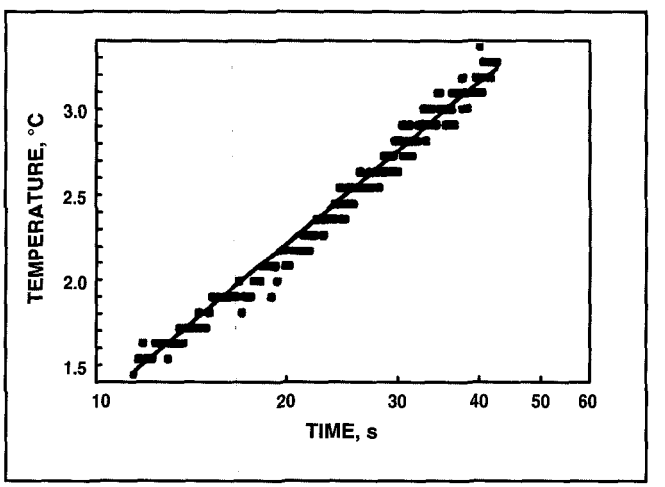


6. Probe construction for measuring thermal conductivity



7. Typical temperature rise of the probe during heating





called the "line source method" or "probe method."

Theory

In the line source method, the thermal conductivity of a material is determined from the thermal response of a heated, long cylindrical probe of small diameter. The schematic of the setup and the probe shown in **Figs. 5 and 6** are similar to those described by Lobo and Claude *(8)*. The 11-cm-long x 0.2-cm-diam. probe contains a heater element (constantan, 0.01-cm diam.) and a J-type thermocouple, which measure the surface temperature midway along the length of the probe. A tape heater wound around the sample is used to bring the fluid and the probe to a uniform temperature. A heat flux of typical, 0.6W, supplied to the probe is measured. From the temperature-time history obtained during heating, the thermal conductivity can be calculated. Tye *(9)* provides an excellent description of the apparatus and errors involved in this method.

Ideally, the setup should be an infinitely long thin heat source placed in an infinite homogenous medium of uniform temperature. The solution of the Fourier equation leads to a transient temperature rise, T, at a distance, r, from the heat source *(9)*:

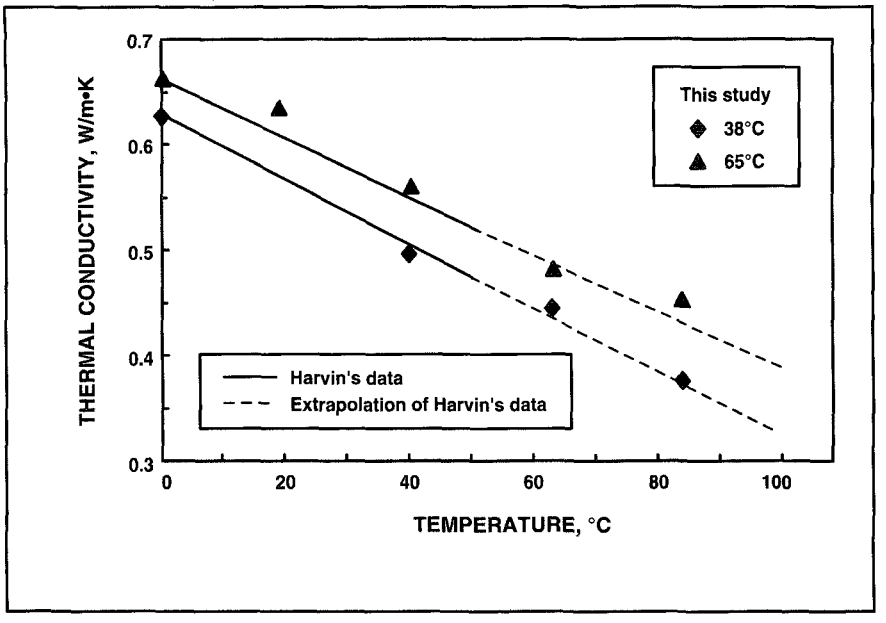
$$T = -\frac{Q}{4\pi\lambda} Z\left(-\frac{r^2}{4\alpha t}\right) \qquad (4)$$

For small values of $(r^2/4\alpha t)$, Eq. 4 can be approximated as:

$$T = \frac{Q}{4\pi\lambda}\left(\ln t + \ln\frac{4\alpha}{r^2} - \gamma\right) \qquad (5)$$

From Eq. 5, it follows that over a time interval $(t\text{-}t_0)$, the temperature rise at a point in the medium is given by:

8. Thermal conductivity of black liquor as a function of solids level at 38°C and 65°C



$$T\text{-}T_o = \frac{Q}{4\pi\lambda} \ln\left(\frac{t}{t_o}\right) \qquad (6)$$

Since Eq. 6 is valid anywhere in the fluid, and thus also at the interface between the fluid and the probe, the heating of the probe surface can also be described by Eq. 6 after an initial transient. To account for the deviations from ideal conditions, Eq. 6 was modified as:

$$T\text{-}T_o = \frac{CQ}{4\pi\lambda} \ln\left(\frac{t}{t_o}\right) \qquad (7)$$

$$T = \frac{CQ}{4\pi\lambda} \ln t + constant \qquad (8)$$

where C is a probe constant. The probe constant was determined to be 0.82 by calibrating the probe in glycerol, a material for which the thermal conductivity is accurately known. With this constant, the thermal conductivity of water was determined as 0.63 W/m·K at 38°C and 0.658 W/m·K at 65°C; both are within 2% of the values published by Perry and Green *(10)*. The above analysis is only valid if natural convection effects can be neglected. These effects are generally neglected when the Grashoff number is less than 10^4. The Grashoff number of the present system was typically between 10^{-2} and 10^2, based on a probe temperature rise of about 3°C and viscosities between 0.8 and 1000 mPa·s.

Results

Figure 7A shows the temperature rise of the probe, T, during the heating period of about 40 seconds. The same data are replotted in **Fig. 7B** against the natural logarithm of time.

The thermal conductivity is calculated from the slope of the straight line through the data in Fig. 7B, obtained by linear regression analysis. The black liquor thermal conductivity was determined as a function of solids level at two temperatures and is plotted in **Fig. 8**. The present data agree well with that of Harvin and Brown *(1)*, who used a measurement technique based on steady-state heat transfer through a slab. The results show that Harvin and Brown's thermal conductivity data can be extrapolated to higher solids levels to predict the thermal conductivity.

Conclusions

For routine measurement of black liquor viscosity in a pulp mill, the rotating spindle viscometer can be used when the free surface exposed to the atmosphere is covered with a thin layer of silicone oil. With this modification, the simple, cheap, rugged Brookfield viscometer gives reproducible and accurate results.

A cylindrical heater/probe technique was successfully used to measure the thermal conductivity of black liquor from 0 to 83% solids, over a temperature range of 24°C to 68°C. The present thermal conductivity data are well described by the correlations of Harvin and Brown, who used liquors with solids concentrations to 53%. Note that the agreement was obtained despite the fact that different liquors were used in the two studies. Hence, the influence of liquor properties cannot be established.

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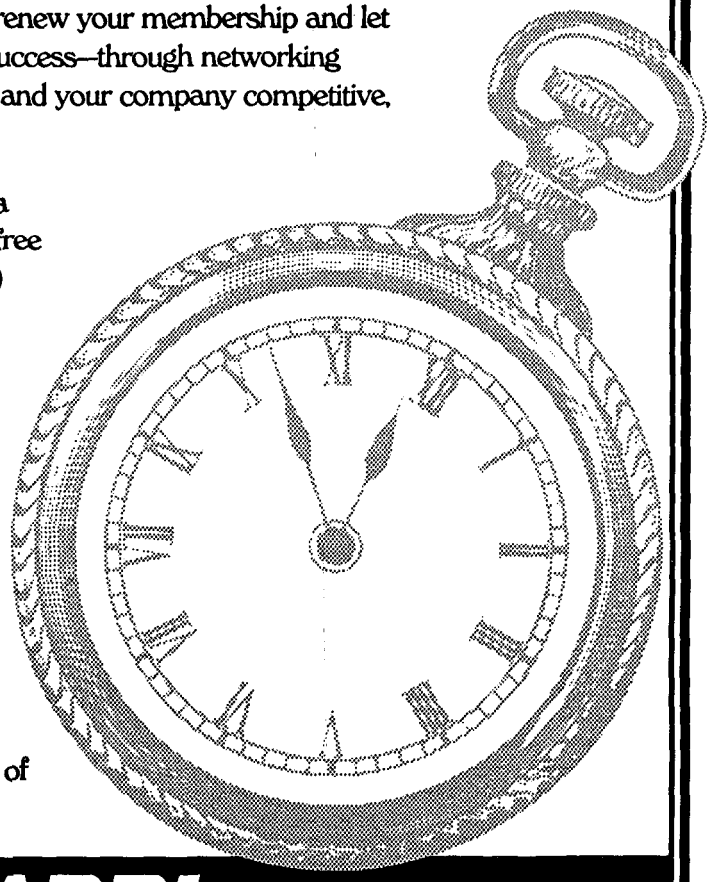
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